

Content and Release of Bisphenol A from Polycarbonate Dental Products

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Bisphenol A (BPA) is an endocrine disruptor, and is used as a raw material for bisphenol A diglycidyl methacrylate and polycarbonate, that are used in the dental materials. In this study, the total and released amounts of BPA from polycarbonate-based dental materials were measured with high-pressure liquid chromatography (HPLC). The specimens used were orthodontic brackets and denture base resins in the same condition as when obtained commercially were cut into 3×3×4 mm pieces and crushed into powder. The HPLC analysis was carried out after immersion of the specimens in water or ethanol for a determined time. The total amount of BPA in the specimens was analyzed after dissolution in chloroform. The amount of BPA released after immersion in water for 1 hr was 0.01–0.4 μg/g for the block samples and 0.14–4.22 μg/g for the crushed samples, while that in ethanol for 1 hr was 0.12–9.42 μg/g for the block samples and 0.42–22.24 μg/g for the crushed samples. The control of BPA in the denture preform resin was 78.9 μg/g and this increased to 90.2 μg/g after heating to form dentures and then to 250 μg/g with mechanical crushing. The results of this study indicate that BPA is released from polycarbonates used in dentistry, and that the thermal conditions during the manufacturing of restorations may cause polymer decomposition resulting in the formation of BPA.

Key words : Bisphenol A, Polycarbonate, HPLC analysis

INTRODUCTION

Recently, endocrine disrupting chemicals have become a social problem of great importance. These types of chemicals enter organisms and act as hormones, inhibiting the mechanism of androgens, and may also influence the secretion of hormones and reproduction.

The relationship between dental materials and endocrine disrupting chemicals was first indicated by Olea *et al.*¹⁾ Bisphenol A (BPA) was detected in the saliva of patients treated with fissure sealants, that were resin based on bisphenol A, as a skeleton. This seemed to cause estrogenic activity. However, there were discrepancies and doubts regarding the sampling method and analysis of the resin composition used in that research^{2–4)}.

Bisphenol A (BPA) is considered to be an endocrine-disrupting chemical, and

although many *in vivo* and *in vitro* experiments have evaluated its effects in organisms, there are still many points to be clarified⁵⁻¹⁰. We must establish if BPA is included in dental materials, if BPA is produced during use via polymer decomposition, and if this BPA is released.

The chemicals with BPA as a skeleton used in dental materials are bisphenol A diglycidyl methacrylate (Bis-GMA), its related chemicals, and polycarbonate (PC). In this study, the release of BPA from PC resin-based orthodontic plastic brackets¹¹ and from injection or heat compression molding denture base resin¹² was evaluated with high-pressure liquid chromatography (HPLC). Also, the total amount of BPA present in one type of denture base resin was calculated with the help of the manufacturer by dissolution of the raw polymer, preform resin and denture base molding products in organic solvents.

MATERIALS AND METHODS

Materials

The materials used in the experiment were orthodontic brackets and injection or heat compression molding denture base resin and molding products (Table 1). Four types of brackets were used: Clear bracket (Sankin), Aesthetic-Line (Forestadent), Silkon ML (American Orthodontics) and Sprit MB (Ormco); and four types of denture base resins: Sumiploy Denture System (Sumitomo Chemicals), Reining System (Toushinyougyou), UB Denture (Ube · Sankin) and PC · preform resin (Sankin.) were selected. The UB Denture was a polysulphonated resin manufactured in 1995.

Specimen Preparation

The brackets were used in the same condition as they are bought commercially (4×3.5×2 mm, with slots of 1×1 mm) and were crushed into a powder using a mortar and a pestle or an agatha planetary ball mill (mortar and agatha ball P-7 type, Fritsch Co., Germany), obtaining 2-4 flakes of 0.2-0.3 mm for each bracket. The preform resin and denture base molding products were also used in two forms, cut

Table 1 Orthodontic brackets and injection or heat compression molding denture base resin used in this study

Material	Manufacturer	Code
Clear bracket	Sankin ¹	CB
Aesthetic-Line	Forestadent ²	AES
Silkon ML	American Orthodontics ³	SB
Spirit MB bracket	Ormco ⁴	MB
Sumiploy Denture System	Sumitomo Chemicals ⁵	Sumi
Reining System	Toushinyoko ⁶	T-Rei
UB Denture	Ube ⁷ · Sankin ¹	UB
PC · Preform	Sankin ¹	PCP

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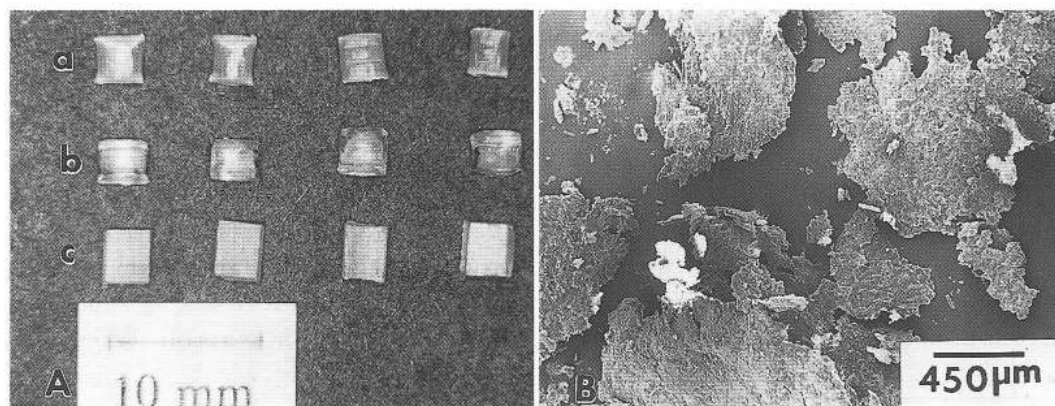


Fig. 1 Heat compression molding denture base resin raw polymer moldings (A; a: with filler, b: without filler, c: preform) and after being crushed into powder (B) used in the experiment.

into $3 \times 4 \times 4$ mm pieces with a low-speed disc or 3.5 mm diameter round pieces before molding (Reining System), and crushed into powder in the same way as the brackets. The PC preform resin (Sankin.) was used after heat compression molding and in 2 raw polymer pellets (with and without fillers) before molding (Fig. 1). The molding was done in a gypsum mold 20 mm in diameter and 4 mm high at a temperature of 240°C for the upper ring and 280°C for the lower ring. Each resin type was crushed manually with a mortar and pestle as described above, and then mechanically using a crushing machine for 5 minutes.

HPCL analysis

Similar amounts (50–100 mg) of the specimens in blocks or powder were immersed in unionized water and 95% ethanol at 37°C for 1 and 5 hours. The released liquid was centrifuged (10,000 rpm) for 10 minutes and the obtained supernatant was analyzed with reverse-phase HPLC (LC-10AS, Shimadzu, Kyoto). The concentration gradient technique was applied for 20 and 60 minutes using an ODS system column, and 40% and 100% acetonitrile as the transference-phase solutions. An ultraviolet-ray detector (SPD-6A, Shimadzu, Kyoto) was used for BPA detection; and a chromatocoder (SIC) was regulated to 225 nm wavelength for analysis.

The part equivalent to the BPA amount after HPLC analysis was measured using a mass analysis machine (VOYAGER ELITE, MALDI/TOF, Perceptive Biosystems, USA) using equal parts of the obtained samples (column: 10 nm of diameter and 250 nm of high) and the already known molecular volume of BPA. The total amount of BPA present in each related compound of the PC preform resin (Sankin) was measured from HPLC analysis of the supernatant after dissolution of 20 mg of each specimen in $200 \mu\text{l}$ of chloroform, addition of $200 \mu\text{l}$ of ethanol and centrifugation (15,000 rpm/10 min.). The amount of BPA released was calculated by weight of the resin volume minus the glassfibers present in the material (Guan *et al.*¹¹⁾).

RESULTS AND DISCUSSION

During HPLC analysis, the BPA on the chromatograph was considered to be similar to the peak of the authentic BPA retention time. The HPLC spectrum for the BPA analysis of the Aestetik-Line bracket is shown in Fig. 2. As shown in the spectrum of Fig. 3, for confirmation, the compounds of the peak area were analyzed for volume and quality, resulting in a value of 228.13, that is similar to BPA (228.10).

The results of BPA release from orthodontic plastic brackets are shown in Table 2. The amount of BPA released from each bracket was 0.01–0.4 $\mu\text{g/g}$ when immersed in unionized water and 0.15–9.42 $\mu\text{g/g}$ when immersed in ethanol. When com-

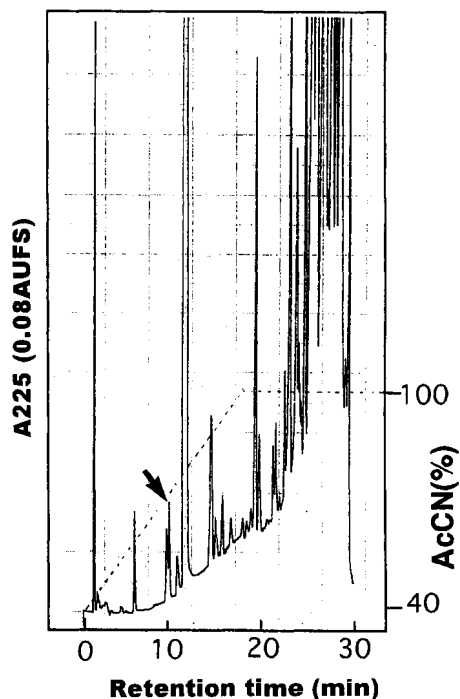


Fig. 2 Chromatogram (HPLC) of an extract from an aesthetic-line bracket.

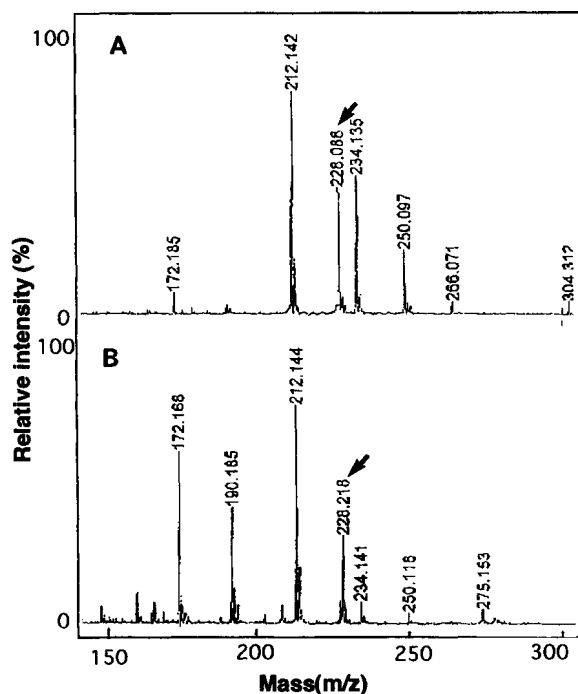


Fig. 3 Mass spectrum of an extract from an aesthetic-line bracket (A) and authentic bisphenol A (B).

Table 2 Amount of BPA released from orthodontic plastic brackets

Code name	Bisphenol A release ($\mu\text{g/g}$)							
	CB		AES		SB		MB	
Solvent*	W	E	W	E	W	E	W	E
Untreated	0.06	0.23	0.16	0.56	0.40	9.42	0.01	0.15
Crushed	0.50	2.54	1.24	6.34	4.22	22.24	1.52	6.09

*W: H_2O ; E: 95% $\text{C}_2\text{H}_5\text{OH}$

paring among the manufactured products, Silkon ML produced the greatest amount of BPA release out of all types of solvents. The difference in the released amount with the use of different solvents may be due to differences in BPA solubility. If BPA dissolves 100% in 95% ethanol, it would dissolve 3.5% in water. After crushing the brackets into powder the amount of BPA released was 0.50–4.22 $\mu\text{g/g}$ when immersed in unionized water and 2.54–22.24 $\mu\text{g/g}$ when immersed in ethanol. This may result from an increase in the surface area of the specimens.

The results of BPA release from the polycarbonate denture base resin are shown in Table 3. The amount of BPA released was 0.01–0.09 $\mu\text{g/g}$ when immersed in unionized water and 0.12–0.21 $\mu\text{g/g}$ when immersed in ethanol. After crushing into powder, the amount of BPA released was 0.14–1.08 $\mu\text{g/g}$ when immersed in unionized water and 0.42–3.24 $\mu\text{g/g}$ when immersed in ethanol. When comparing among the manufactured products, UB produced the lowest amount of BPA release compared to Sumi, T-Rei and PCP. This was probably because UB is a polysulphonate resin¹³⁾ with about half of the molecule formed by a diphenylsulphon group, having a higher thermal stability when compared to polycarbonates, leading to a lower amount of free BPA being included.

According to the results of the release tests above, a partial BPA release from the PC is assumed. The total BPA amount present in the PC was analyzed for the product of only one manufacturer, because the synthesis method of PC is common for all manufacturers and this one offered the raw polymer used during the manufacturing process.

The immersion time was defined by the results of previous experiments; for up to 1 hour of immersion the released amount was large, but after that there were just small changes.

Table 3 Amount of BPA released from injection or heat compression of molding denture base resin

Code name	Bisphenol A release ($\mu\text{g/g}$)							
	Sumi		T-Rei		UB		PCP	
	W	E	W	E	W	E	W	E
Untreated	0.06	0.14	0.09	0.14	0.01	0.21	0.03	0.12
Crushed	1.08	2.97	0.34	3.24	0.14	0.42	0.56	—

*W: H₂O; E: 95% C₂H₅OH

Table 4 Amount of BPA content and release from polycarbonate when immersed in distilled water at 37°C for 1 or 5 hours

Bisphenol A ($\mu\text{g/g}$)	Raw polymer		Preform	Product	Crushed product		
	Without filler	With filler			Manual	Mechanical	
Content	20.7	147.4	78.9	90.2	165.6	250.8	
Release	1 hr	0.11	0.06	0.03	0.06	0.56	8.06
	5 hr	0.14	0.09	0.06	0.10	0.71	13.89

The total amount and the amount after dissolution in unionized water of BPA release from the polycarbonate type denture base resin (Sankin.) are shown in Table 4. The total amounts of BPA released from the 2 types of preform resin raw polymers (with and without fillers) were 147.4 and 20.7 $\mu\text{g/g}$, respectively; the polymer with fillers showing a greater amount. This may be due to the heat (260°C/30 min.) produced during the inclusion of fillers, leading to thermal decomposition of the polymer and producing BPA. The filler present in the raw polymer was 12wt% potassium aluminum system. The BPA content in the preform resin (78.9 $\mu\text{g/g}$) may be a consequence of preparing by mixing two types of polymers in a ratio of 1:1. The amount of BPA present in the products manufactured using the preform resin (90.2 $\mu\text{g/g}$) may be due to the thermal decomposition during manufacturing, but the effect of hydrolysis with the water present in the gypsum form was not clear. The products crushed manually showed 165.6 $\mu\text{g/g}$ of BPA, a value that increased to 250.8 $\mu\text{g/g}$ after mechanical crushing. This could be due to the stress during crushing and partial temperature rise, leading to the polymer's thermal decomposition¹⁴⁾, and producing BPA.

The amount of BPA released from blocks of preform resin and its raw polymers was 0.03–0.11 $\mu\text{g/g}$, which increased after crushing, especially after mechanical crushing when the amount of release was 8.06 $\mu\text{g/g}$. The longer the period of immersion in unionized water, the greater the amount of BPA released. However, as the total amount of BPA in the polymer is small, the amount of BPA released from polycarbonates in the intraoral environment is very small.

CONCLUSIONS

Analysis of total and released amounts of BPA from polycarbonate-based products such as orthodontic brackets and denture base materials resulted in the following conclusions:

- 1) During the synthesis of polycarbonates, non-reacted BPA remains inside the materials and is released when they are immersed in water or organic solvents.
- 2) As for polycarbonates, the thermal conditions (temperature, time, etc) during the inclusion of fillers and fabrication of restorations lead to polymer decomposition and BPA production.

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REFERENCES

- 1) Olea, N., Pulgar, R., Perez, P., Olea-Serrano, F., Rivas, A., Novillo-Fertrell, A., Pedraza, V., Soto, A. M. and Sonnenschein, C.: Estrogenicity of resin-based composites and sealants used in dentistry, *Environ Health Perspect* **104** : 298-305, 1996.
- 2) Ashby, J.: Bisphenol-A dental sealants, The inappropriateness of continued reference to a single female patient, *Environ Health Perspect* **105** : 362, 1997.
- 3) Nathanson, D., Lertpitayakun, P., Lamkin, M. S., Edalatpour, M. and Chow, L. L.: *In vitro* elution of leachable components from dental sealants, *J Am Dent Assoc* **128** : 1517-1523, 1997.
- 4) Imai, Y.: Comments on the paper "Estrogenicity of resin-based composites and sealants used in dentistry" by Olea *et al.* (1), *Environ Health Perspect* **107** : A290, 1999.
- 5) Krishnan, A. V., Stathis, P., Permuth, S. F., Tokes, L. and Feldman, D.: Bisphenol-A: An estrogenic substance is released from polycarbonate flasks during autoclaving, *Endocrinology* **132** : 2279-2286, 1993.
- 6) Steinmetz, R., Brown, N. G., Allen, D. L., Bigsby, R. M. and Ben-Jhonathan, N.: The environmental estrogen bisphenol A stimulates prolactin release *in vitro* and *in vivo*, *Endocrinology* **138** : 1780-1786, 1997.
- 7) Nagel, S. C., vom Saal, F. S., Thayer, K. A., Dhar, M. G., Boechler, M., Welshons, W. V.: Relative binding affinity-serum modified access (RBA-SMA) assay predicts the relative *in vivo* bioactivity of the xenoestrogens bisphenol A and octylphenol, *Environ Health Perspect* **105** : 70-76, 1997.
- 8) Vom Saal, F. S., Cooke, P. S., Buchanan, D. L., Palanza, P., Thayer, K. A., Nagel, S. C., Parmigiani, S. and Welshons, W. V.: A physiologically based approach to the study of bisphenol A and other estrogenic chemicals on the size of reproductive organs, daily sperm production, and behavior, *Toxicol Ind Health* **14** : 239-260, 1998.
- 9) Schafer, T. E., Lapp, C. A., Hanes, C. M., Lewis, J. B., Wataha, J. C., Schuster, G. S.: Estrogenicity of bisphenol A and bisphenol A dimethacrylate *in vivo*, *J Biomed Mater Res* **45** : 192-197, 1999.
- 10) Cagen, S. Z., Waechter Jr, J. M., Dimond, S. S., Breslin, W. J., Butala, J. H., Jekat, F. W., Joiner, R. L., Shiotuka, R. N., Veenstra, G. E. and Harris, L. R.: Normal reproductive organ development in CF-1 mice following prenatal exposure to bisphenol A, *Toxicol Sci* **50** : 36-44, 1999.
- 11) Guan, G., Takano-Yamamoto, T., Miyamoto, M., Hattori, T., Ishikawa, K. and Suzuki, K.: Shear bond strengths of orthodontic plastic brackets, *Am J Orthod Dentofacial Orthop* **117** : 438-443, 2000.
- 12) Suzuki, K.: Denture base resin of heat compression molding type, *J Dent Technol* **23** : 188-197, 1995. (in Japanese)
- 13) Brandrup, J. and Immergut, E. H.: Polymer hand book, 2nd ed., John Wiley & Sons, New York, 1975, pp. III 166-167.
- 14) Tomikawa, M.: Studies on polycarbonate II, Decomposition of polycarbonate, *High Polymer* **20** : 102-107, 1963. (in Japanese)