Studies on the radiopacity of experimental dental composite resins containing admixed SiO_2–ZrO_2 fillers

M. TAIRA, H. TOYOOKA, H. MIYAWAKI, M. YAMAKI
Department of Dental Materials, Hiroshima University School of Dentistry, Hiroshima-shi 734, Japan

To produce radiopaque silica (SiO_2)-based fillers, zirconia (ZrO_2) powders were mechanically added to SiO_2 powders with ZrO_2 content up to 40 wt%. We evaluated the radiopacity of experimental composite resins consisting of (Bis–GMA + TEGDMA + CQ + DMAEMA) monomer mixture (25 wt%) and admixed SiO_2–ZrO_2 fillers (75 wt%), and compared their radiopacity with those of human dentin and enamel. It became confirmed that the radiopacity of experimental composite resins increased linearly with zirconium content, while the composite resin containing 80 wt% SiO_2–20 wt% ZrO_2 filler possessed radiopacity similar to that of human enamel. It was proved that the radiopacity of the composites could be precisely controlled by adjusting ZrO_2 content in SiO_2–ZrO_2 fillers.

1. Introduction

Visible-light-cured (VLC) dental composite resins have been widely accepted as restorative materials due to their aesthetic merits and ease in handling [1]. Daily dental clinics, further, request that they should be radiopaque so that dentists can distinguish a restoration from caries, evaluate voids, improper contour and overhangs in restorations, and diagnose secondary caries adjacent to the restorations [2–4].

Radiopacity of composites usually results from the incorporation of an element of relatively high atomic number, such as barium and strontium, into the SiO_2-based filler particles [5]. Because the fillers widely vary in their size, content and composition [6, 7], the radiopacity of commercial VLC dental composites currently used considerably differ from brand to brand [8–12].

Although barium is the strongest radiopacifier for SiO_2 glass [5], barium ions, once leached out into the oral fluid, are potentially hazardous to the oral soft tissues [13]. Therefore, it seems clinically beneficial to prepare radiopaque SiO_2-based fillers which are biologically safer. Although zirconium is a chemically inert [14] and effective radiopacifier for SiO_2-based glass [15], there have been few studies to actually examine the radiopacity of composite resins containing SiO_2–ZrO_2 fillers [15].

The purpose of this investigation was, therefore, to prepare self-formulated VLC composite resins containing admixed SiO_2–ZrO_2 fillers, and evaluate their radiopacity in contrast to those of human dentin and enamel.

2. Materials and methods

2.1. Formulation of VLC composite resin pastes containing admixed SiO_2–ZrO_2 fillers

To prepare admixed SiO_2–ZrO_2 fillers having ZrO_2 contents of 0 wt %, 10 wt %, 20 wt %, 30 wt % and 40 wt %, commercially pure ZrO_2 powder (Wako Junyaku Co., Osaka, Japan; Lot no. = ECN2428; mean particle size = 5.9 μm) were, successively, weighed with an electric balance (Libror AEL-2000, Shimadzu Co., Kyoto, Japan) and mechanically mixed with commercially pure SiO_2 powder (Wako Junyaku Co., Osaka, Japan; Lot no. = LKJ3319; mean particle size = 10.56 μm), using a pestle and a mortar.

The monomer mixture consisted of 59.5 wt % Bisphenol A glycidyl dimethacrylate (D-GMA, Shin-Nakamura Co., Wakayama, Japan) (Bis-GMA), 39.5 wt % triethyleneglycol dimethacrylate (Tokyo Kasei Co., Tokyo, Japan) (TEGDMA), 0.5 wt % camphorquinone (Tokyo Kasei Co., Tokyo, Japan) (CQ) and 0.5 wt % dimethylaminoethyl methacrylate (Tokyo Kasei Co., Tokyo, Japan) (DMAEMA). For simplicity, the composite containing 80 wt % SiO_2–20 wt % ZrO_2 filler was denoted here as 20 wt % ZrO_2 composite.

VLC composite pastes were prepared by mixing 25 wt % monomer mixture and 75 wt % admixed SiO_2–ZrO_2 fillers with a pestle and a mortar.

2.2. Evaluation of radiopacity of the composites containing admixed SiO_2–ZrO_2 fillers and extracted human teeth

Five experimental composite pastes were packed into Teflon moulds 6 mm in diameter and 1, 2 and 3 mm thick, respectively, both ends of the moulds were covered with plastic sheets and slide glasses, and the pastes were photo-cured for 40 s each from two directions with a VL source (Quicklight model VL-1, Morita Co., Kyoto, Japan). Freshly extracted human teeth were mounted in cold-cured polyester resin blocks (Rigolac, Showa Koubunshi Co., Tokyo, Japan), and cut longitudinally into sections 1 and 2 mm thick including areas of both dentin and enamel, respectively, with a slow-speed diamond saw (ISOMET, Buhler, Co., Evanston, Ill., USA). Three samples of each material were prepared in this study.

To measure radiopacity, each set of specimens were placed on ultraspeed dental X-ray films (DF57, Eastman Kodak Co., NY, USA), along with an aluminum wedge having 16 steps ranging from 1.0 to 16.0 mm. The specimens were then radiographed using a calibrated dental X-ray source (Supermax 70, Morita Co., Kyoto, Japan) and a standardized technique. An X-Ray unit was operated at 70 kVp and 8 mA with a focus-film distance of 26.5 cm, and an exposure time of 0.4 s. The radiographic density of each material in developed films was measured with a transmission densitometer (DENSICON model HAD-301, Hiranuma Sangyo Co., Ibaragi, Japan). The radiopacity of the test specimens were then expressed in terms of equivalent aluminum-thickness (mm) by reference to the calibration curve for the radiographic density of the aluminum step-wedge (Fig. 1).

3. Results

Table I shows raw data of the radiopacity of five experimental composite resins containing admixed SiO_2–ZrO_2 fillers, human dentin and human enamel, expressed as equivalent aluminum-thickness (mm).

Fig. 2 shows the effects of the ZrO_2 content in the fillers on the radiopacity of the composites containing admixed SiO_2–ZrO_2 fillers. It became evident that the addition of the ZrO_2 content in the fillers lead to the linear increment in the radiopacity of the composites, and there existed a trend that the thicker the sample of composite, the greater the radiopacity. We also found strong linear correlations between ZrO_2 content (wt %) in the filler (X) and the radiopacity of the composite (equivalent aluminum-thickness, mm) (Y), as follows:

For 1 mm thick composites, $Y = 0.602 + 0.107X$ ($r = 0.987$)

For 2 mm thick composites, $Y = 0.784 + 0.197X$ ($r = 0.986$)

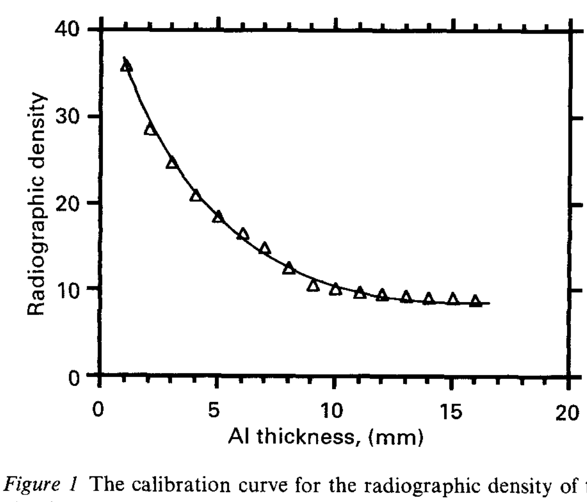

Figure 1 The calibration curve for the radiographic density of the aluminum step-wedge.

TABLE I Radiopacity of self-formulated composite resins containing admixed SiO_2–ZrO_2 fillers, human dentin and human enamel, expressed as equivalent aluminum-thickness (mm) (mean $\pm$ standard deviation, $n = 3$)

Sample	Sample thickness (mm)		
	1	2	3
100 wt% SiO_2 composite	0.93 ± 0.09	1.33 ± 0.12	1.77 ± 0.33
10 wt % ZrO_2 composite	1.23 ± 0.40	1.90 ± 0.43	3.27 ± 0.52
20 wt % ZrO_2 composite	2.73 ± 0.37	4.83 ± 0.50	7.80 ± 0.28
30 wt % ZrO_2 composite	3.83 ± 0.34	6.90 ± 0.37	10.60 ± 0.96
40 wt % ZrO_2 composite	4.97 ± 0.24	8.70 ± 0.36	13.20 ± 0.92
Human dentin	1.00 ± 0.26	1.90 ± 0.17	
Human enamel	2.43 ± 0.21	4.13 ± 0.21	

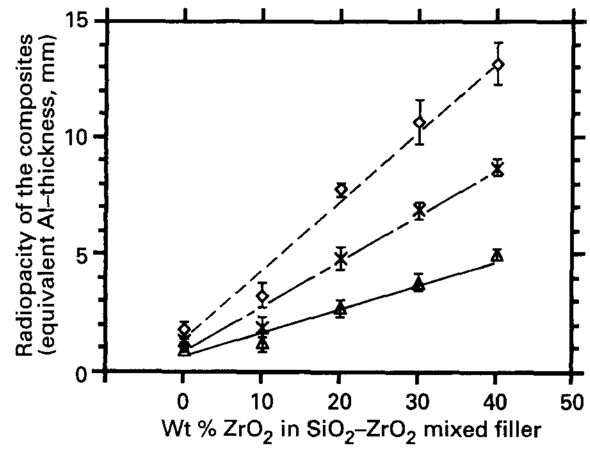

Figure 2 The effects of the ZrO_2 content in the fillers on the radiopacity of five experimental composite resins containing admixed SiO_2–ZrO_2 fillers: △ 1 mm; × 2 mm; ◇ 3 mm.

For 3 mm thick composites, $Y = 1.290 + 0.303X$ ($r = 0.991$)

where r is the linear regression coefficient.

Fig. 3 is the three-dimensional comparison of the radiopacity of the composite specimens, human dentin and human enamel. It became clear that 100 wt % SiO_2 composite was virtually radiolucent, 10 wt % ZrO_2 composite had the weak radiopacity similar to that of human dentin, 20 wt % ZrO_2 composite displayed the intermediate radiopacity analogous to that of human enamel, and 30 wt % ZrO_2 composite and 40 wt % ZrO_2 composite possessed the strong radiopacity exceeding that of human enamel.

4. Discussion

This study confirmed that the radiopacity of the experimental composite resins containing admixed SiO_2–ZrO_2 fillers covered those of human dentin and enamel, and could be easily and precisely controlled by adjusting the ZrO_2 content in the filler. It appears clinically beneficial to provide radiopacity-adjustable VLC composite resins. The rationale for this statement is described below.

Council on Dental Materials, Instruments and Equipment [3] recommend that a requirement for radiopacity be included in ADA (American Dental Association) specification No. 27 for direct filling

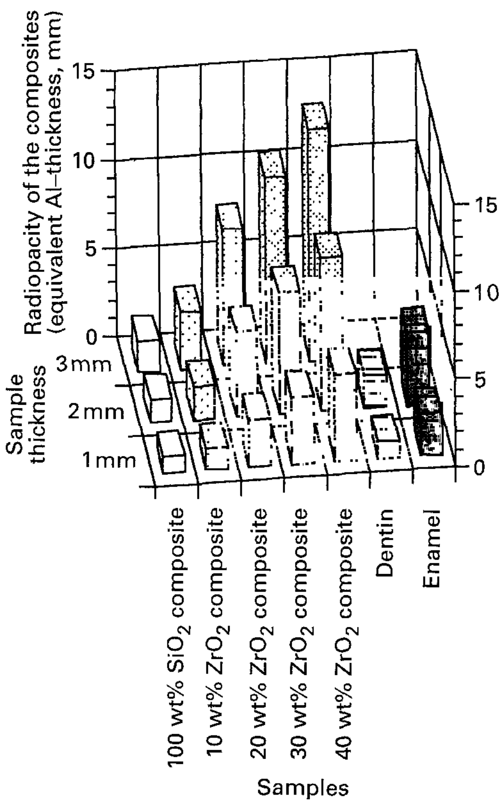

Figure 3 Three-dimensional comparison of the radiopacity of five experimental composite resins containing admixed SiO_2–ZrO_2 fillers, human dentin and human enamel.

resins. The required level of the radiopacity for the composite is, however, not standardized, yet [8]. A higher radiopacity of the composite provides easier distinction of the filling (e.g. helpful for the detection of swallowed fillings) [8]. On the other hand, it has been reported that semi-radiopaque composite having the radiopacity slightly in excess of that of human enamel provides the best condition for radiographic detection of caries and defects, adjacent to restoration, compared with very radiopaque materials such as amalgam and gold alloys [4]. It is also known that human dentin and enamel have a wide variety of radiopacity, dependent upon the age, site and condition of caries [16]. Because the radiopacity level of the target human enamel differs, dependent upon each individual, it seems clinically useful to provide radiopacity-adjustable composites.

To produce aesthetic dental composite resins with their colour quality matching well with neighbouring human teeth, most often SiO_2-based powders have been selected as the filler for the composites. Although composites containing admixed SiO_2–BaO fillers have the radiopacity, slightly greater than those of the composites containing admixed SiO_2–ZrO_2 fillers, the latter fillers appear to be clinically more advantageous due to their chemical inertness and biological safety.

Because of the large difference in the refractive index among SiO_2 powder, ZrO_2 powder and monomer mixture and resultant extensive light scattering phenomenon, the light transmittance through the composites containing admixed SiO_2–ZrO_2 fillers are limited, leading to the short depth of cure. In the near future, it is expected to prepare chemically homogeneous SiO_2–ZrO_2 fillers [17] so that the depth of cure of the composites containing SiO_2–ZrO_2-based fillers could be increased.

5. Conclusions

We fabricated VLC composite resin discs, 1, 2 and 3 mm thick which contained admixed SiO_2–ZrO_2 fillers with ZrO_2 content up to 40 wt %, and evaluated their radiopacity with respect to those of sliced human dentin and enamel, 1 and 2 mm thick. It became apparent that the radiopacity of the composite increased linearly with increasing ZrO_2 content in the filler, and that generally the thicker the composite, the greater the radiopacity. It was pointed out that the radiopacity of the composite could be precisely controlled by adjusting ZrO_2 content in the said fillers.

References

1. J. R STURAVANT, T F LUNDEEN, T. B Jr SLUDER, A D WILDER and D. F TAYLOR, *Dent. Mater.* **4** (1988) 105
2. Z SHEY and M OPPENHEIM, *J. Amer. Dent. Assoc.* **98** (1979) 569.
3. Council on Dental Materials, Instruments and Equipments, *J. Amer. Dent. Assoc.* **102** (1981) 347.
4. I ESPELID, A B TVEIT, R L ERICKSON, S C KECK and E A GLASSPOOLE, *Dent. Mater.* **7** (1991) 114.
5. D C. WATTS, *J. Dent.* **15** (1987) 38.
6. H HOSODA, T YAMADA and S INOKOSHI, *J. Prosthet. Dent.* **64** (1990) 669.
7. A M KHAN, H SUZUKI, Y NOMURA, M TAIRA, K WAKASA, H SHINTANI and M YAMAKI, *J. Oral Rehabil.* **19** (1992) 361.
8. C M. STANFORD, P L FAN, C. M SHOENFELD, R KNOEPPEL and J. W. STANFORD, *J. Amer. Dent. Assoc.* **115** (1987) 722.
9. J W V. van DIJKEN, K R. WING and I E. RUYTER, *Acta. Odontol. Scand.* **47** (1989) 401.
10. T. GOSHIMA and Y GOSHIMA, *Dentomaxillofac. Radiol.* **18** (1989) 19.
11. E G FARMAN, *Oral Surg. Oral Med. Oral Path* **70** (1990) 226.
12. G WILLEMS, J NOACK, S INOKOSHI, B. LAMBRECHTS, B van MEERBEEK, M BRAEM, J F. ROULET and G. VANHERLE, *J Dent.* **19** (1991) 362.
13. R L BOWEN and G W CLEEK, *J. Dent. Res.* **51** (1972) 177.
14. M NOGAMI, *Yougyou Kyoukai-shi* **93** (1985) 195 (in Japanese).
15. C P. MABIE and D L MENIS, *J Biomed. Mater. Res.* **12** (1978) 435.
16. J A WILLIAMS and R W BILLINGTON *J. Oral Rehabil.* **14** (1987) 267.
17. K KAMIYA, S MABE, T YOKO and K TANAKA, *Nippon Seramikkusu Kyoukai Gakujutsu Ronbunshi* **97** (1989) 229.

Received 23 April 1993 and accepted 21 January 1994