

Influence of chlorine dioxide on the physical properties of denture base materials

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Purpose: The purpose of this study was to determine the influence of chlorine dioxide (ClO₂) on the physical properties of commercial denture base materials.

Materials and Methods: One heat-polymerized denture base acrylic resin and three metallic materials; gold-silver-palladium alloy, pure titanium, and cobalt-chromium (Co-Cr) alloy, were used in the study. Three types of commercial denture cleansers Polident (POL), Pika (PIK), and Kirari (KIR) were used. And ClO₂ was used at the following three concentrations: 1, 10, and 100 ppm. The flexural strength and flexural modulus of denture base resin were measured using universal testing machine. And the colour stability and surface morphology of dental metal materials were measured using colorimeter and scanning electron microscope.

Results: Flexural strength of the resin blocks was 70 MPa or more for all denture cleanser after 90 days of immersion. The flexural modulus was greater than 2,000 MPa specified in ISO standards for all test specimens. The specimens of Co-Cr immersed in ClO₂ exhibited high values after immersing for 90 days at 10 ppm and for all immersing times at 100 ppm concentration.

Conclusion: The following conclusions were drawn: 1) low concentrations of ClO₂ cause less discoloration than commercially available denture cleansers; and 2) low concentrations of ClO₂ are suitable for use as denture cleanser. (Asian Pac J Dent 2013; 13: 27-35.)

Key Words: chlorine dioxide, denture base resin, denture cleanser, metallic material

Introduction

Currently, life expectancy of individuals in Japan is the longest in the world, with the percentage of elderly individuals in the population exceeding more than the 14% defined by the United Nations to indicate the elderly society. In 2012, a Cabinet Office survey found that the rate of aging was 24.1%, indicating that Japan was now a super-aging society (<http://www8.cao.go.jp/kourei/whitepaper/index-w.html>), and the aging population is expected to continually increase in the future at a rate unseen elsewhere in the world. Many elderly individuals wear dentures, with the proportion of denture wearers known to increase in late-stage elderly individuals. Promotion of the 8020 movement has seen a reduction in the number of missing teeth, but it has been reported that the number of elderly individuals requiring dentures will increase in the future.

The ability to comfortably continuously use dentures is very important for the maintenance and improvement of the quality of life in the elderly, and denture maintenance is an essential element in denture comfort. However, the cleaning process, which is a pivotal part of denture maintenance, is often not correctly performed, leaving many dentures clearly dirty. Reasons for this include the fact that cleaning is often performed by staff other than dentists or dental hygienists at long-term healthcare facilities and hospitals, and many facilities are inadequately staffed. It has also been reported that denture plaque-derived microorganisms can easily enter the denture base resin and cause infections with symptoms such as denture stomatitis.^{1,2} Consequently, we believe that denture cleaning and denture plaque control are not being ideally conducted.

There are two methods of cleaning dentures, chemical cleaning and mechanical cleaning.^{3,4} Chemical denture cleaning is performed using a denture cleanser, the active ingredient of which is a disinfectant that kills microorganisms and cleans the dentures. For mechanical cleaning, denture brushes and ultrasonic cleaning

devices are used to mechanically remove microorganisms and stains from the denture surface. Because mechanical cleaning should be manually performed, many elderly individuals find it difficult to correctly execute this, particularly those who require care. Despite this, it is extremely important for elderly individuals that both the intraoral cavity and dentures are kept clean in order to prevent serious conditions such as aspiration pneumonitis. Therefore, the use of denture cleaning preparations is indispensable.

Currently, commercially available denture cleaning preparations can be divided according to their active ingredient into peroxides, enzymes, acids, hypochlorous acids, Ag^+ -apatite, and crude drug.⁴ All these preparations are widely used to suppress colony formation of *Candida*-type fungi such as *Candida albicans* and to prevent and remove denture plaque formation.⁴⁻⁹ However, there is evidence that the daily use of denture cleaning preparations can affect the physical properties and mechanical nature of the denture base resin.¹⁰⁻¹⁵ Moreover, it has been reported that alkaline components such as NaOH contained in some denture cleaning preparations can cause rust and discoloration of the metal parts of the dentures.¹⁶⁻¹⁸

Although hypochlorous acid offers the greatest bactericidal effects, denture cleanser, in which this is the active ingredient are almost all exclusively used by dentists, strong metal corrosive effects have also been reported.¹⁷ The most commonly used commercially available denture cleaning preparations contain peroxides such as H_2O_2 as their active ingredient. Alkaline chemicals are considered to have harmful effects on the denture materials, while neutral chemicals are reported to have poor stain removal effects. Moreover, enzymes are reported to have few harmful effects on denture materials and are suitable as a tissue conditioner or for cleaning soft lining material but have poor cleaning effects.^{4,9} It has also been reported that denture cleanser can be accidentally consumed by the elderly who suffer from reduced decision-making ability,¹⁹ suggesting that preparations containing active ingredients that are safer for humans are required.

Taking all the above into account, we focused on chlorine dioxide (ClO_2) as a possible active ingredient for a new type of denture cleanser. ClO_2 is used as a disinfectant for the highly virulent influenza virus and was approved as the first food additive with oxidizing disinfectant properties in the 218th ordinance of the Ministry of Health, Labor and Welfare, which was a partial revision of standards for food additives (370th ordinance of the Ministry of Health, Labor, and Welfare) released in 1994. Because it is very safe, it is used to treat drinking water. Previous studies in the literature regarding ClO_2 have shown that its high oxidizability offers greater antibacterial effects and faster treatment times than chemicals such as NaOCl and H_2O_2 .²⁰⁻²¹ However, very few studies have investigated the effects of ClO_2 on denture base materials.

Thus, the present study investigated the effects of ClO_2 , as a novel active ingredient in denture cleanser, on physical properties of denture base resin and cast surface color stability of the following three types of metallic materials: 12% gold-silver-palladium alloy (Para), pure titanium (CpTi) and cobalt–chromium alloy (CoCr).

Materials and Methods

Table 1 shows the commercial denture cleansers used in this study. A total of three types were used, peroxide-type Polident (POL), hypochlorous acid-type Pika (PIK), and titanium dioxide-type Kirari (KIR).

When using the denture cleaning solutions, we used one tablet or one packet of each solution dissolved in 150 mL of distilled water. We also used distilled water as control. ClO_2 was used at the following three concentrations: 1, 10, and 100 ppm. Commercially available denture cleaning solutions were changed daily, while the ClO_2 solutions were changed weekly.

Table 1. Commercial denture cleansers used in this study

Code	Material	Type	Manufacturer
Con	Distilled water		
POL	Polident	Peroxide	Glaxo Smith Kline K.K.
PIK	Pika (Red)	Hypochlorite	Rohto Pharmaceutical Co., Ltd.
KIR	Kirari	Titanium dioxide	Nissin Dental Products Inc.

Effects on physical properties of denture base resin

One heat-polymerized acrylic denture base resin (live pink with fiber; Acron, GC Co., Tokyo, Japan) was used. Rectangular blocks (65×10×3 mm) of denture base resin were polymerized according to the manufacturer's recommended procedures. After polymerization the specimens were stored in distilled water for 24 hours at 37°C. The surfaces of the specimens were abraded with 1,200 grit waterproof abrasive paper, scrubbed with tap water and air-dried. Five specimens were immersed into each denture cleanser solutions for 24 hours at 23±2°C.

After immersion in each denture cleanser solutions for 0, 1, 2, 14, 30, and 90 days, the flexural strength, flexural modulus, and flexural deflection of each specimens were measured according to the ISO20795-1 recommended procedures,²² using universal testing machine (Instron5565, Instron Co., Canton, MA, USA). All data were analyzed by one-way and three-way analysis of variance (ANOVA) with a Tukey's multiple comparison test at a 5% level of significance.

Effects on surface properties of metallic materials

Table 2 shows the metallic materials used in this experiment. We used the following three types of metals commonly used in removable prosthodontic devices: cobalt-chromium alloy (CoCr), 12% gold-silver-palladium alloy (Para), and pure titanium (CpTi). The metal samples (20×10×2 mm) were cast according to the manufacturer's directions. Only one side of each specimen was mirror polished. A total of 21 specimens were prepared, and three pieces of each were immersed in each of the denture cleanser solutions for 24 hours at 23±2°C.

Table 2. Metallic materials used in this study

Code	Material	Type	Components (%)	Manufacturer
Para	Cast Master 12L	Gold-silver-palladium	Ag 48, Pd 20, Cu 17, Au 12, Others 3	IDS Co., Ltd.
CpTi	8020 Pure Titan	Pure titanium	Ti 99.3, Others 0.07	Shimizutech Co., Ltd.
CoCr	Dan-cobalt	Cobalt-chromium	Co 60.7, Cr 31.3, Mo 6, Others 2	Nihon Shika Kinzoku Co., Ltd.

After immersion in the denture cleanser solutions for 30, 60, and 90 days, color changes were measured with a colorimeter (CR-321, Konica Minolta Optics Co., Tokyo, Japan) and evaluated using the CIE L*a*b* color system.²³ The CIE L*a*b* color system is based on three parameters for defining color: L*, a*, and b*, where L* stands for lightness, a* for redness-greenness, and b* for yellowness-blueness. The individual white color index of the instrument was used as a color control, according to the manufacturer's instructions. The color change (ΔE^*) of each specimen was calculated as follows: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.²³

The specimen surfaces were also observed using a scanning electron microscope (SEM; JSM-639LA, JEOL Ltd., Tokyo, Japan). All data were analyzed by one-way and three-way ANOVAs with a Tukey's multiple comparison test at a 5% level of significance.

Results

Effects on physical properties of denture base resin

Figure 1 shows changes over time in the flexural strength for each specimen. Flexural strength of the resin blocks was 70 MPa or more for all denture cleansers after 90 days of immersion. However, at the end of the 90 days' immersion, flexural strength value was decreased than that before immersion for all denture cleansers. Nevertheless, flexural strength after 90 days' immersion in the ClO_2 solution was greater than 65 MPa specified in ISO standards for denture base resin.

Figure 2 shows changes over time in flexural modulus. The flexural modulus was greater than 2,000 MPa specified in ISO standards for all specimens. Figure 3 shows changes over time in the flexural deflection. No significant differences indicated for any of the denture cleansers over the 90 days' immersion period compared with pre-immersion values.

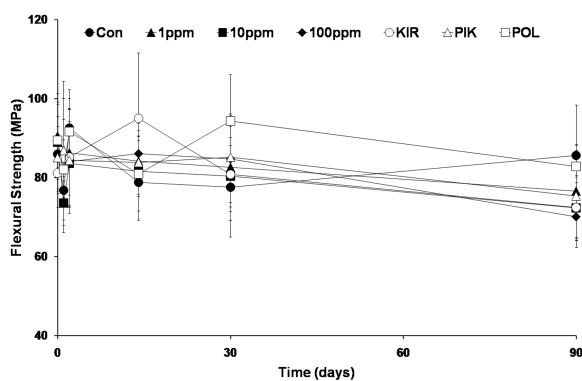


Fig. 1. Variations in flexural strength with immersion time

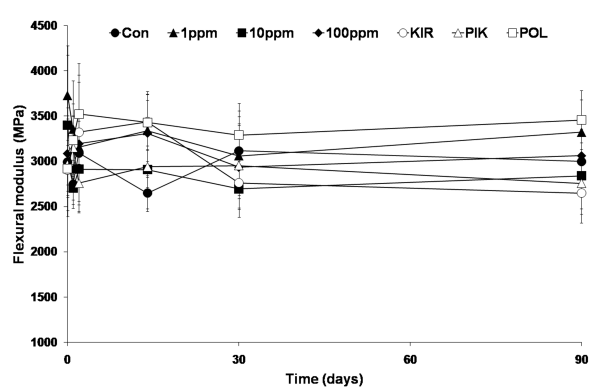


Fig. 2. Variations in flexural modulus with immersion time

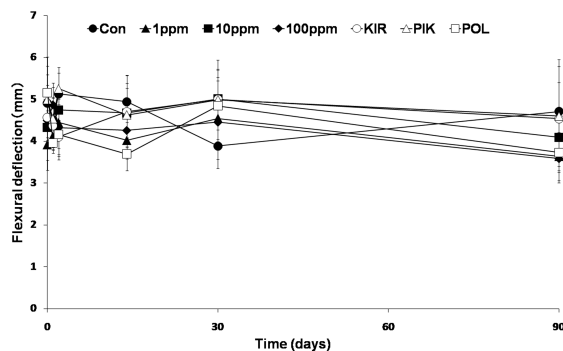


Fig. 3. Variations in flexural deflection with immersion time

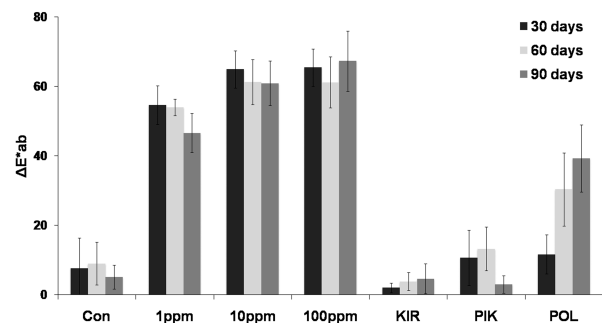


Fig. 4. ΔE^*ab of Para with standard deviation after immersion

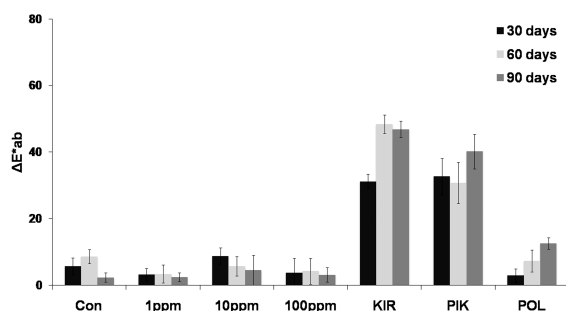


Fig. 5. ΔE^*ab of CpTi with standard deviation after immersion

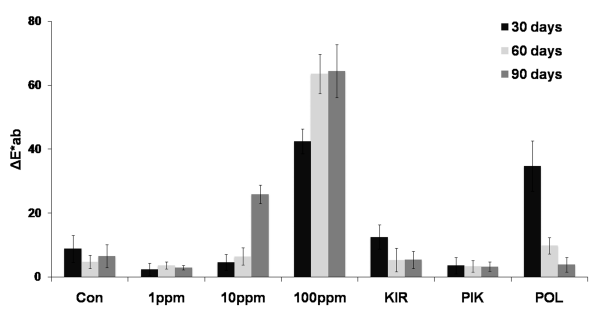


Fig. 6. ΔE^*ab of CoCr with standard deviation after immersion

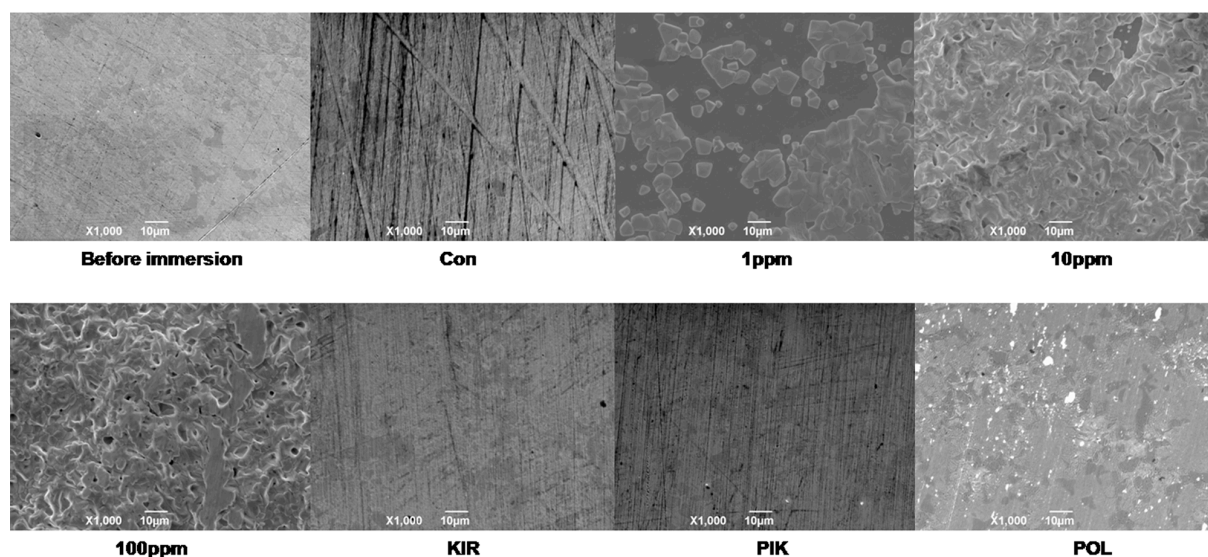


Fig. 7. SEM image of Para after immersion 90 days

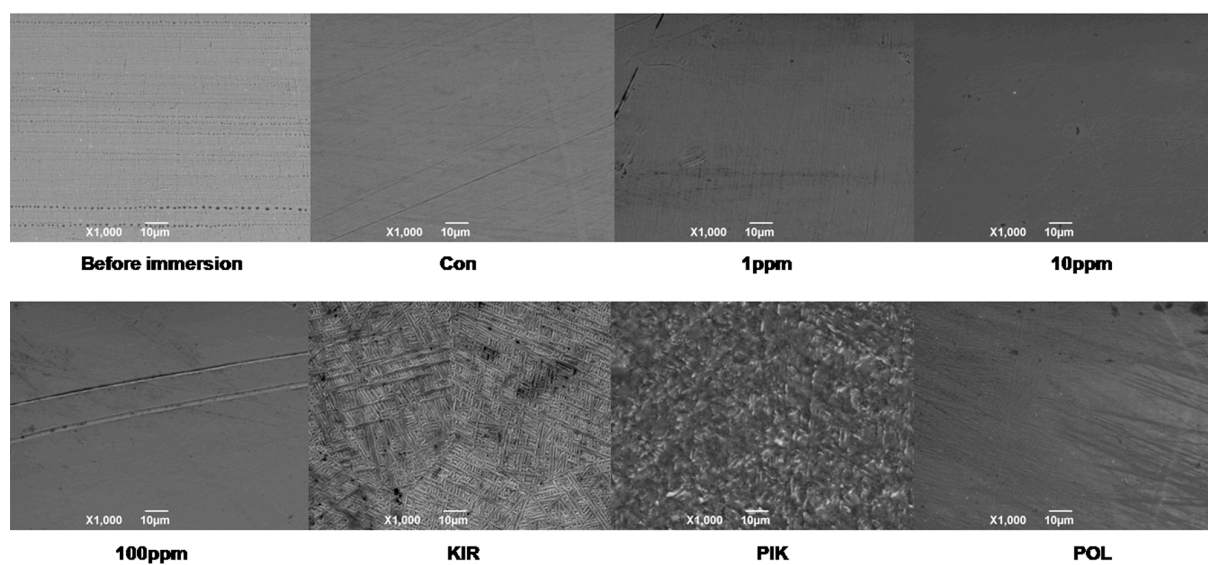


Fig. 8. SEM image of CpTi after immersion 90 days

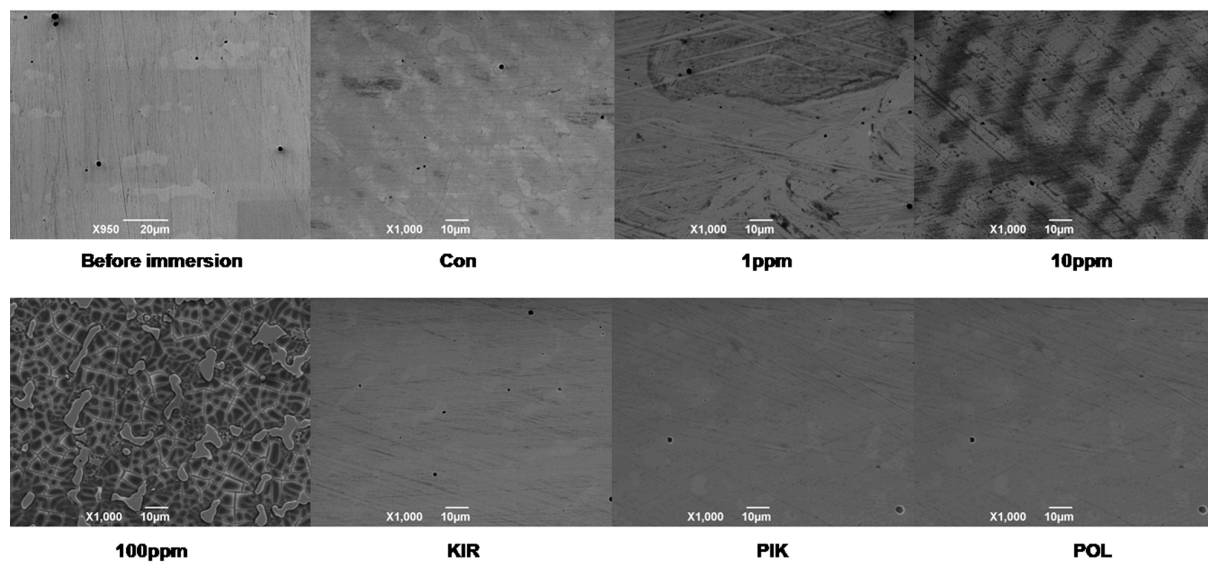


Fig. 9. SEM image of CoCr after immersion 90 days

Effects on surface properties of metallic materials

Figures 4, 5, and 6 show the ΔE^*ab values for each specimen. After immersing in ClO_2 and POL solutions, the ΔE^*ab values of Para were higher than those of any other denture cleansers as well as commercially available denture cleansers at all concentrations and all immersion times. With CpTi, the specimens immersed in PIK and KIR exhibited high ΔE^*ab values for all immersion times. No significant differences were indicated between any other denture cleanser solutions or immersion times. CoCr specimens exhibited high ΔE^*ab values after being immersed for 30 days in POL. The specimens immersed in ClO_2 exhibited high values after immersion for 90 days at 10 ppm and for all immersion times at 100 ppm concentration.

Figures 7, 8, and 9 show SEM images for each specimen. No marked changes were observed in any of the metal parts immersed in distilled water. All Para specimens immersed in ClO_2 exhibited surface roughness, which tended to become more marked with increasing concentrations between 1-100 ppm. The surfaces of Para specimens immersed in POL exhibited more marked surface roughness than those immersed in KIR or PIK. The surfaces of CpTi specimens immersed in KIR and PIK exhibited more marked roughness than the other types. CoCr specimens immersed in ClO_2 exhibited marked roughness at concentrations of 10 and 100 ppm.

Figure 10 shows the energy dispersive X-ray spectrometry (EDX) results for the surfaces of specimens of Para immersed for 90 days in ClO_2 . The Cl and Ag were detected in the specimen surfaces at all concentrations.

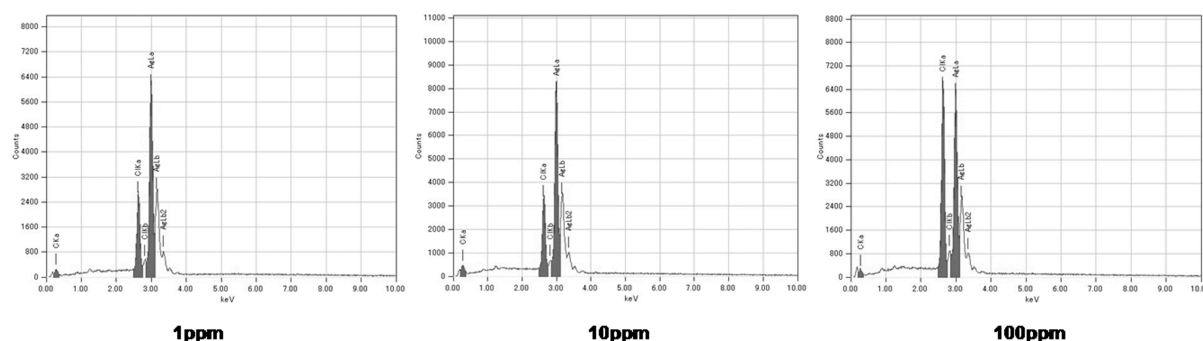


Fig. 10. EDX results of Para in day 90 immersed in ClO_2

Discussion

Denture cleansers are widely used clinically as an effective method for preventing and removing denture plaque formation.^{4,6,8,9} However, the continued use of these preparations may result in the deterioration of the denture base materials.^{7,8} It has been reported that the high oxidizability of ClO_2 offers greater antibacterial effects than chlorine-based disinfectants, and it is better than hypochlorous acid at removing bacteria stuck to the denture base resin.²⁴ However, no reports have investigated the effects of ClO_2 on the denture base materials. Longevity of the denture base materials is an important problem in prosthodontics. In the prosthodontics clinic, the mechanical attributes and color stability of a prosthesis may be the two of the most important factors determining a patient's acceptance. Therefore, in the present study we investigated the effects of ClO_2 on the physical properties of denture base resin and metallic materials.

Denture base resin is known to deteriorate with long-term clinical use, and it is possible that denture cleaning could also affect this deterioration. It has been indicated that when mechanically cleaning dentures with a denture brush, there is a risk that excessive brushing pressure could cause abrasion.²⁵ Furthermore, it has also been indicated that the long-term use of denture cleansers to chemically clean dentures can also cause their

deterioration.^{14,26} Many reports in the literature of studies that evaluated the effects of denture cleansers on the denture base resin have used color differences as a basis for assessment.^{14,26,27} However, the resin flexural characteristics are the most important elements to be taken into consideration with regard to the clinical use of this material.²⁸ The present study evaluated changes over time in the denture base resin flexural strength and flexural modulus in accordance with the ISO20795-1²² international standards.

The present study found that the flexural strength values of the resin specimens reduced following 90 days of immersion in all denture cleanser solutions compared with the pre-immersion values. This may have been because the flexural strength of resin specimens reduced when heat-polymerization type denture base resin absorbed water while immersion.^{29,30} However, both the flexural strength and flexural modulus values met ISO standards for the denture base resin following treatment with all denture cleanser solutions. Although during normal use, dentures would be immersed in the denture cleanser for approximately 12 hours, the experiments conducted in the present study involved a 24 hours immersion cycle, making this study an accelerated test. Consequently, the results are equivalent to over 6 months' immersion in the denture cleansers, suggesting that ClO_2 could be suitable for use as a denture cleanser.

To assess the effects on metallic materials, the present study investigated discoloration caused by immersion in the denture cleansers. The esthetic appearance of dental appliances is an important issue in clinical dentistry. In particular, color stability is one of the most important factors affecting patients' acceptance of prosthetic appliances. Furthermore, because color stability is used as a scale to assess corrosion in metal parts, it is an important element to evaluate the durability of the metallic materials. Discoloration of the metallic materials involves loss of gloss and development of surface pigmentation caused by surface roughness because of corrosion and formation of corrosion products. This study examined discoloration caused by the denture cleanser in CoCr, Para, and CpTi metal parts. The CIE $L^*a^*b^*$ color system to assess discoloration, used in this study, is widely used to evaluate color changes and discoloration, and it can express the extent of discoloration in numerical values.²³ Metal discoloration is said to be generally caused by changes on the metal surface involving the formation of a thin film of sulfide, oxide, or chloride materials, leading to corrosion, after which the alloy reacts to its surrounding environment and degrades over time.¹⁶⁻¹⁸

The present experiment revealed that immersion in ClO_2 caused little color change in CpTi but strongly affected Para and tended to affect CoCr depending on the concentration. It has been previously indicated that titanium develops corrosion and discoloration in the presence of fluorine ions.^{18,31} Here we found that CpTi exhibited strong discoloration when soaked in PIK and KIR. Because PIK and KIR solutions are alkaline,^{4,9} our results were consistent with the findings of Been¹⁸ who reported that alkaline solutions cause discoloration of titanium. Been also conducted surface analysis after immersion in alkaline hydrogen peroxide and reported that marked roughness and formation of oxides were noted in the surface of specimen that exhibited discoloration.¹⁸ In the present study, the results of the SEM observation clearly indicated surface roughness and intergranular corrosion in CpTi immersed in PIK and KIR, suggesting a correlation. It is known that the passivation film, TiO_2 , can form on the surface layer of titanium, and our results suggest that TiO_2 had formed on the surfaces of CpTi immersed in PIK and KIR, which exhibited strong color changes.

Currently, the gold-silver-palladium alloy is not commonly used in metal denture parts, but it was used in the present study for comparison with titanium and cobalt-chromium alloy. Gold-silver-palladium alloy is generally known to be prone to discoloration and corrosion. The fact that unlike titanium and cobalt-chromium alloy, the

gold-silver-palladium alloy, which does not exhibit passivation, may be affecting color changes and surface roughness. We also observed marked discoloration in the specimen immersed in ClO_2 , with SEM images revealing marked surface roughness and surface precipitate buildup. The results of analysis with EDX detected Cl and Ag, with the Ag derived from Para reacting with the Cl present in the ClO_2 solution. This suggests that discoloration is caused by the formation of silver chloride.

The cobalt-chromium alloy is the most commonly used material for metal denture parts. Overall, we found that it exhibited smaller color changes than other metal types. SEM observation indicated no significant surface roughness except when immersed in ClO_2 at a concentration of 100 ppm. This may have been because chromium easily forms a passive oxide film.¹⁷

The results of the present study suggest that the color stability of metallic materials can be greatly affected by denture cleaning preparations depending on their constituent metal. We also found a tendency for more marked discoloration with increased immersion time of the metallic materials. However, the effects of denture cleansers differed according to the type of metallic materials, suggesting that differences in the components of the metallic materials were causing these differences in effects.

Although the present study involved immersion metallic material specimen in denture cleanser for 24 hours, in actual clinical practice, patients are instructed not to immerse metal prosthetic appliances in the denture cleansers for long periods of time (no more than 1 hours). Furthermore, instructions for some denture cleansers suggest immersion metal prosthetic appliances for short periods of time (5-30 minutes). Accordingly, using denture cleansers with compatible metallic materials and following directions for the use of such preparations can minimize discoloration, which usually leads to corrosion of metal components.

According to our results, ClO_2 at concentrations of 1 and 10 ppm causes less discoloration than commercially available denture cleansers, except when used on Para. ClO_2 exhibits sufficiently effective antibacterial action within the pH range of pH 3-8,³² and previous studies have shown that when used as an active ingredient in the denture cleansers, approximately 5 ppm offers adequate antibacterial effects. Consequently, we believe that ClO_2 can be used as a denture cleaning preparation for denture base materials.

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