

Self-cleaning Ability of a Photocatalyst-containing Denture Base Material

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Received December 6, 2006/Accepted September 14, 2007

This study examined the ability of a photocatalyst mixed in a denture base resin to decompose organic substances which adhered to the denture base resin surface. The photocatalyst was mixed with denture base resin at concentrations of 0, 5, 10, and 15% (w/w). Decomposition test, bending test, and surface roughness measurement were performed at 1, 7, 30, 90, and 180 days after polymerization. Decomposition ability was evaluated based on the residual amount of methylene blue (MB) dissolved in ethanol after UV irradiation for 12 hours. As the mixing ratio increased, the amount of MB in the solution decreased. Meanwhile, no changes in the amount of MB in the immersion solution were observed in the photocatalyst-free resin specimen. Therefore, the results indicated that a denture base resin containing a photocatalyst might have a photocatalytic ability.

Keywords: Decomposition ability, Denture base material, Photocatalyst

INTRODUCTION

It is established that good oral health care can improve the quality of life, especially in preventing denture stomatitis and general diseases in the elderly¹⁻⁴. However, this improvement in quality of life and self-confidence is not experienced and enjoyed by many denture wearers. This is because many of them suffer from poor oral health owing to their failure to keep their dentures clean — despite expressed instructions by the dentist or oral hygienist to clean their dentures carefully⁵. On the prevalence of denture wearers with poor dental health, the root causes seem to stem from the complicated shapes of the dentures and the roughness of the mucosal surface^{6,7}.

Microorganisms easily accumulate on the mucosal surface of dentures and which cannot be easily removed through mechanical polishing⁸. It has been reported that the occurrence of denture stomatitis and/or yeast adhesion on the mucosal surface of dentures are closely related to the degree of cleanliness of the dentures, but not to the frequency of denture brushing or method of denture cleaning⁹. Further, this report highlighted the difficulty of effective denture plaque removal. Therefore, to improve the oral health of denture wearers, it is necessary to develop a simple and effective method to remove denture plaque.

In the current environmental catalyst market, the photocatalyst has attracted considerable attention¹⁰⁻¹². In particular, titanium dioxide (TiO₂) is well

known as a stable photocatalyst. Radicals are generated upon ultraviolet light irradiation on TiO₂. These radicals oxidize organic substances into water and carbon dioxide. Calcium hydroxyapatite (HAP) is also an interesting biomaterial because of its capacity to adsorb organic substances¹³. An atomic-level composition of a photocatalytic material and HAP has been realized by modifying calcium hydroxyapatite particles with Ti(IV)¹⁴. This resulting material possesses both intense photocatalytic ability and adsorption affinity.

Leveraging on the encouraging outcome of the abovementioned photocatalytic composite material, we speculated that the incorporation of a photocatalyst to the denture base material might likewise generate radicals and effectively remove denture plaque. In this manner, denture base materials are conferred with a self-cleaning ability.

The aim of this study, therefore, was to examine the ability of a photocatalyst mixed in a denture base material to decompose organic substances. If positive research findings were yielded, this material would indeed make denture cleaning easier for a wide spectrum of beneficiaries: elderly persons, institutionalized patients, caregivers, and healthcare professionals.

MATERIALS AND METHODS

Specimen preparation

The materials used in this study included an auto-

polymerizing polymethyl methacrylate-methyl methacrylate (PMMA-MMA)-based denture base resin (POUR RESIN, Shofu Inc., Kyoto, Japan) and a photocatalyst (HAP modified with Ti(IV), PHOTOHAP, Taihei Chemical Industrial Co. Ltd., Osaka, Japan). PHOTOHAP was a photocatalyst that consisted of white particles measuring 3.78 μm in diameter, with a specific surface area of 41.59 m^2/g . The composition at the site of Ca(II) in the hydroxyapatite was changed to Ti(IV) in this material¹⁴. Next, 0.45, 0.9, and 1.35 g of photocatalyst powder was added to 5 ml of denture base resin liquid. The liquid mixtures were then mixed with 8.55, 8.1, and 7.65 g of resin powder respectively, thus resulting in concentrations ranging in from 0, 5, 10, and 15% (w/w) of photocatalyst powder/denture base resin powder.

The resin paste was placed in putty-type silicon rubber molds ($10 \times 65 \times 2.5 \text{mm}$), which were then sandwiched by glass plates. After polymerization for 20 minutes at 55°C under 0.4 MPa air pressure, specimens were finished by polishing with 1500-grit wet sandpaper.

At one day after polymerization, test specimens were placed into test tubes filled with 10 ml of distilled water and then irradiated with ultraviolet rays (FL15BLB, Toshiba Co., Tokyo, Japan) at a distance of 30 cm (352 nm, 0.4 mW/cm^2) for 12 hours per day. This was repeated for durations of each 7, 30, 90, and 180 days to examine the effects of UV irradiation on denture base resin (Group L). Test tubes were made of borosilicate glass (Asahi Techno Glass Co., Tokyo, Japan) which could transmit light at or above 340 nm wavelength, and its transmission rate was over 80%. Distilled water was changed daily after irradiation.

For polymerized specimens in the one-day group, they were not irradiated before the decomposition test, surface roughness measurement, or bending test. Similarly, another set of test specimens were placed in a dark box and treated in the same manner as those in group L, but without irradiation (Group D). Five specimens were used for each experiment of the decomposition test, resulting in a total of 200 specimens. Another set of test specimens were prepared for the bending test and also surface roughness measurement, where mixing, polymerization, and polishing were performed in the same manner as for the decomposition test. Five specimens were used for each experiment, thus resulting in a total of 200 specimens.

Photocatalytic ability determination

Photocatalytic ability was estimated based on the decomposition of methylene blue (MB; Wako Pure Chemical Industries Ltd., Osaka, Japan). MB is an organic dye which is decomposed by oxidization. Therefore, this dye was considered to be a suitable

model pollutant material to examine the decomposition ability of photocatalysts¹⁵. After each irradiation session, test specimens were immersed in 10 ml of 0.01 mM MB in ethanol solution for three hours. Our preliminary experiments demonstrated that the adsorption amount of MB on specimen surface reached a peak at three hours after immersion in MB solution.

In group L, specimens in the MB solution were irradiated by ultraviolet rays (352 nm) at a distance of 30 cm (0.4 mW/cm^2) for 12 hours. Conversely, specimens in group D were not irradiated after immersion in MB solution. MB solution was placed in a disposable cell made of polystyrene (Kartell, Noviglio, Italy). Absorbance at 650 nm of MB solution was measured with a spectrophotometer (UV-1600PC, Shimadzu Co., Kyoto, Japan) after irradiation.

To evaluate the durability of decomposition ability, the decomposition rate was calculated using following equation:

$$\text{DR} = [(A - A_a)/A] \times 100$$

where "DR" is the decomposition rate, "A" is absorbance of 0.01 mM MB solution, and "A_a" is the absorbance of MB after irradiation.

Surface roughness measurement

Surface roughness was measured before the bending test using the same specimens. It was performed using an accurate three-dimensional laser scanning system (XA100, Ono Sokki, Yokohama, Japan). Linear scanning at 6 mm range was performed at three different positions on specimen surface. The z-value, which corresponded to surface roughness, was automatically calculated by an attached computer system.

Bending test

A three-point bending test was performed to evaluate the mechanical strength of the specimens using a bending test machine (Japan Mecc Co., Tokyo, Japan) (Fig. 1). Test specimen was supported by steel bars at both ends which were 50 mm apart, and mechanical strength was applied at the center of specimen. Loads of 5.0 N were added every minute until failure occurred. Deflection values and loads were recorded until the specimens broke. The fractured surface of specimens was observed using a scanning electron microscope (JSM LV5000, JEOL Ltd., Tokyo, Japan).

Water absorption and solubility tests

Another set of five resin disks (50 mm diameter, 0.5 mm thickness) containing 0, 5, 10, and 15% photocatalyst were prepared for the water absorption and solubility tests. Mixing, polymerization, and polish-

ing were performed in the same manner as those in the previous experiments. The specimens were placed in a desiccator for 24 hours at 37°C, and then transferred to another desiccator for 1 hour at 23°C. This drying procedure was repeated until the weight

change was less than 0.5 mg per 24 hours, at which time the weight of the specimens were measured (W_1).

Specimens were then placed in distilled water for 24 hours to absorb water, after which the weight (W_2) was again measured. Water absorption (P) was calculated according to the equation below¹⁶⁾:

$$P = (W_2 - W_1) / S$$

where “ S ” refers to the total surface area of test specimen.

Specimens were again dried in the same manner as in the absorption test. Weight of the specimens were again measured (W_3). Following which, solubility (Q) was calculated according to the equation below¹⁶⁾:

$$Q = (W_1 - W_3) / S$$

Statistical analysis

All data were analyzed using one-way ANOVA and Scheffe’s multiple range test at a significance level of $p < 0.01$.

RESULTS

Decomposition ability

Figure 2 shows the absorbance levels of MB solutions with photocatalyst-containing specimens. It could be

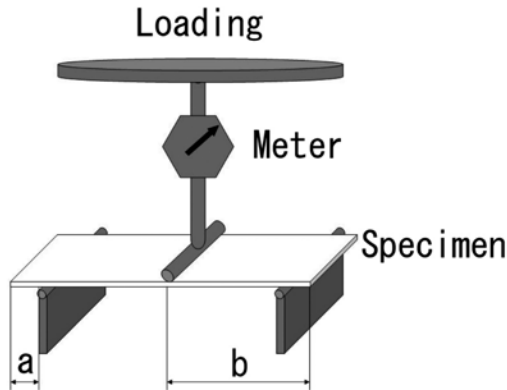


Fig. 1 Schematic drawing of a three-point bending test, where a: distance from edge of specimen to the supporting point at 7.5 mm; b: distance from edge of specimen to the loading point at 32.5 mm.

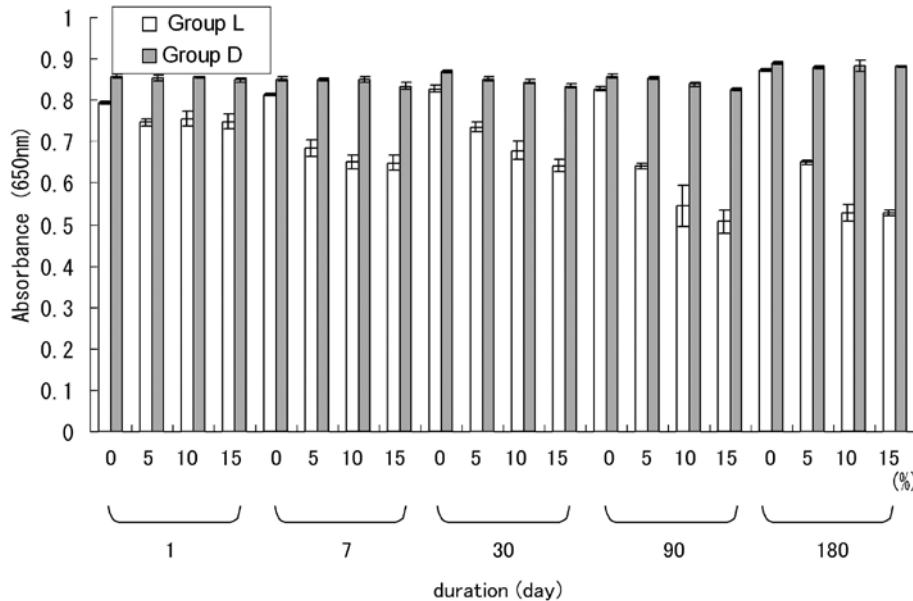


Fig. 2 Absorbance at 650 nm of MB solutions with specimens containing 0, 5, 10, and 15% of photocatalyst after irradiation. There were significant differences between groups L and D. There were significant differences between photocatalyst-free specimen (0%) and specimens containing 5, 10, and 15% of photocatalyst at 7, 30, 90, and 180 days after polymerization in group L. Significant differences among the specimens in group L were further observed as follows: 7days5% versus 7days10% and 7days15%; 30days5% versus 30 days10% and 30days15%; 30days10% versus 30days15%; 90days5% versus 90days10% and 90days15%; 90days10% versus 90days15%; 180days5% versus 180days10% and 180days15% ($p < 0.01$).

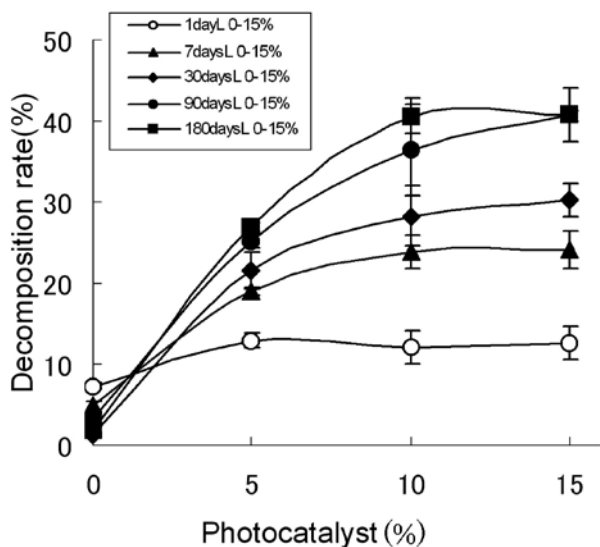


Fig. 3 Decomposition rates of specimens containing 0, 5, 10, and 15% of photocatalyst at 1, 7, 30, 90, and 180 days after polymerization.

seen that their levels were significantly lower than the corresponding photocatalyst-free specimens. This finding indicated that MB on specimen surface was decomposed by the photocatalyst mixed in the denture base resin. In group L, a decreased absorbance level of MB was concomitant with increase in the mixing ratio of photocatalyst. Meanwhile, no significant changes were shown in group D.

As for the decomposition rate, it increased with an increase in the mixing ratio of photocatalyst (Fig. 3). It increased as the length of irradiation period increased, except for the specimen containing 15% of photocatalyst. The decomposition rate of the specimen containing 15% of photocatalyst at 180 days after polymerization did not clearly increase.

Surface roughness

There were no significant differences in surface roughness among the specimens containing the photocatalyst (0, 5, 10, and 15%). There were also no significant differences between groups L and D (Fig. 4).

Bending test

The breaking loads of specimens decreased as the mixing ratio of the photocatalyst increased (Fig. 5). Scanning electron microscopic observations of the fractured surfaces showed many PMMA particles in the specimens containing 10 and 15% of photocatalyst. On the other hand, a compact surface with

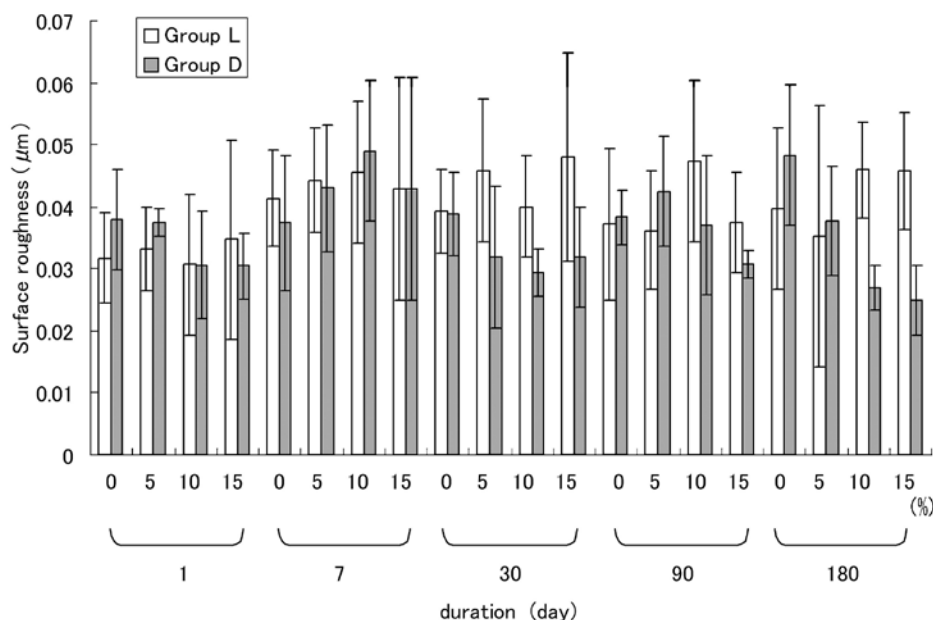


Fig. 4 Surface roughness of specimens containing 0, 5, 10, and 15% of photocatalyst at 1, 7, 30, 90, and 180 days after polymerization. There were no significant differences among the specimens.

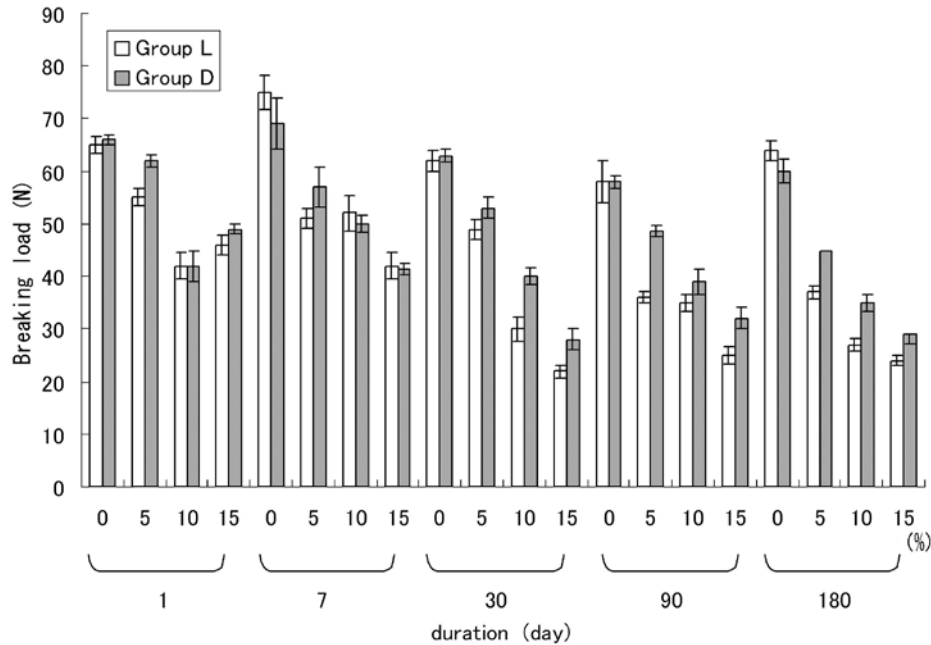


Fig. 5 Breaking loads of specimens containing 0, 5, 10, and 15% of photocatalyst at 1, 7, 30, 90, and 180 days after polymerization. There was significant difference between 90days5% in group L and 90days5% in group D. Significant differences were also observed among the following specimens in group L: 1day0% versus 1day10% and 1day15%; 1day5% versus 1day10%; 7days0% versus 7days5%, 7days10%, and 7days15%; 30days0% versus 30days5%, 30days10%, and 30days15%; 30days5% versus 30days10% and 30days15%; 90days0% versus 90days5%, 90days10%, and 90days15%; 180days0% versus 180days5%, 180days10%, and 180days15%; 180days5% versus 180days15% ($p < 0.01$).

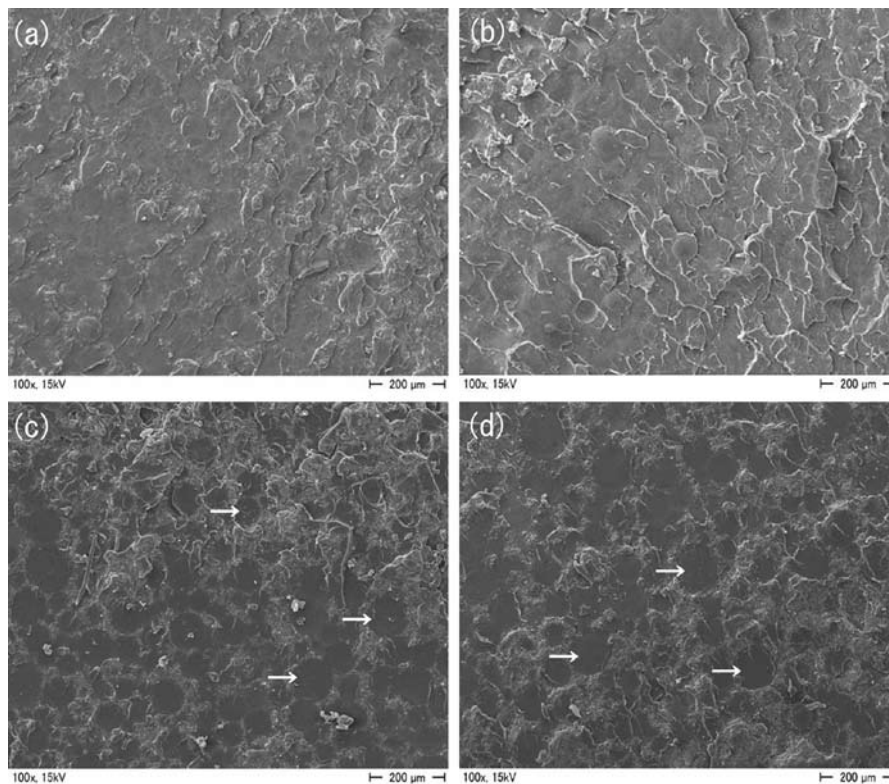


Fig. 6 SEM images of the fractured surfaces of specimens containing: (a) 0%, (b) 5%, (c) 10%, and (d) 15% of photocatalyst at 30 days after polymerization. Many PMMA particles (arrows) were observed in the specimens containing 10 and 15% of photocatalyst.

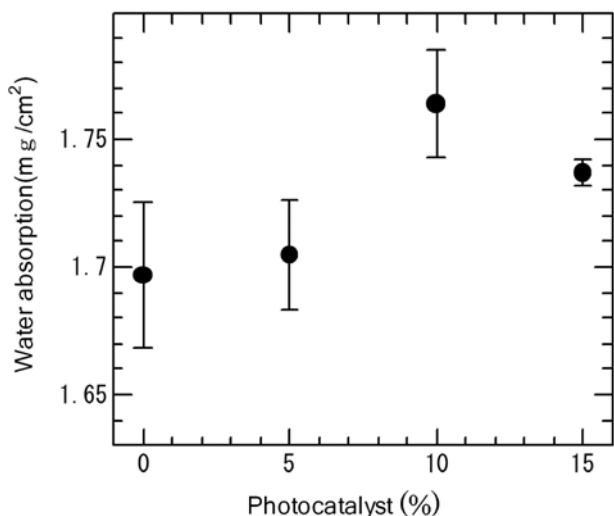


Fig. 7 Water absorption values of specimens containing 0, 5, 10, and 15% of photocatalyst. There were no significant differences among the specimens.

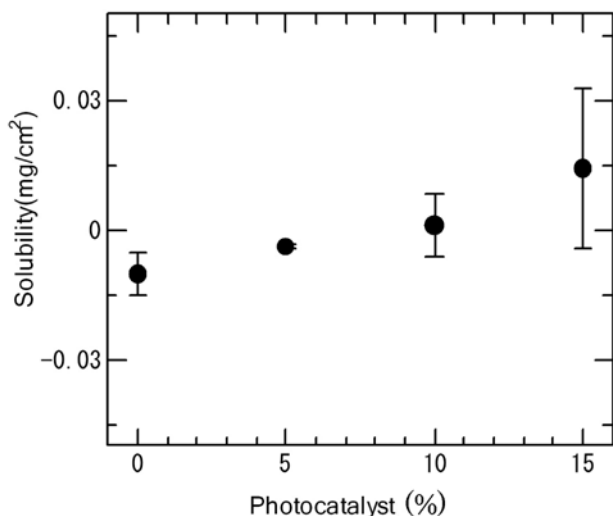


Fig. 8 Solubility values of specimens containing 0, 5, 10, and 15% of photocatalyst. There were no significant differences among the specimens.

shallow depressions was revealed in specimens containing 0 and 5% of photocatalyst (Fig. 6).

Water absorption and solubility

In terms of water absorption, there were no significant differences among the specimens (Fig. 7). In terms of solubility, there were also no significant differences among the specimens (Fig. 8).

DISCUSSION

The chief aim of this study was to develop and examine a denture base resin with a self-cleaning ability. Although this study was only a preliminary experiment, encouraging results were obtained in that the photocatalytic ability and decomposition rate were maintained up to 180 days. Moreover, both values increased with time. Therefore, the photocatalyst used in this study kept its photocatalytic ability regardless of the duration of the experiment.

Previously, many investigations were carried out to combine antifungal or antiseptic agent with denture base resins or soft liners to keep the dentures clean. However, the cleaning effect did not persist for long periods because the antifungal and antiseptic agents were rapidly released from the denture base resins or liners¹⁷⁻²¹. Conversely in this study, the photocatalyst did not leach out from the denture base resin. As a result, the photocatalytic ability was maintained for a long time as shown in Fig. 3. Based on this finding, it could be said that the non-eluting property of the photocatalyst would be useful to developing a denture base resin with a self-cleaning ability.

It is noteworthy that the absorbance levels of MB solutions with photocatalyst-containing specimens in group L were significantly lower than the corresponding levels in group D (Fig. 2). This result might be caused by ultraviolet irradiation which degraded MB in the solution. As for the role of the photocatalyst in the denture base material, it was thought to have accelerated the degradation of MB on the specimen surface.

Surface roughness was not affected by the presence of the photocatalyst nor by the use of ultraviolet irradiation. This showed that photocatalyst-containing resin might be useful as a denture base material.

However, mechanical strength decreased as the ratio of the photocatalyst increased. In particular, the mechanical strength substantially decreased at 30, 90, and 180 days after polymerization. The ensuing reduction in mechanical strength was suggested to be due to ultraviolet irradiation. However, no significant differences were observed between groups L and D except at 90 days 5%. Therefore, the amount of photocatalyst that was contained in the resin was the dominant factor in the reduction of mechanical strength.

Kanie *et al.* reported that when γ -methacryloxypropyltrimethoxysilane was added to PMMA resins to increase the adhesive strength to porcelain tooth, the flexural strength of the PMMA resins decreased²². They reported that this was due to inhibited polymerization. In this study, the volume ratios of MMA/PMMA in the photocatalyst-containing specimens were larger than that of photocatalyst-free speci-

men. This might have resulted in an increase in the amount of residual monomer. Further, scanning electron microscopy showed many PMMA particles on the fractured surfaces of photocatalyst-containing specimens. The photocatalyst did not dissolve in MMA, and was thought to remain around PMMA. As the photocatalyst neither combined with PMMA nor the resin matrix, a reduction in mechanical strength ensued. Taken together, the reduction in mechanical strength was suggested to have been caused by both the amount of photocatalyst contained in the resin and the residual monomer.

The decomposition rate increased as the length of irradiation period increased. This result might be caused by the decomposition of denture base resin by photocatalysis. As a result of the decomposition of denture base resin, many photocatalyst particles were exposed on the surface. However, there were no significant differences in surface roughness between groups L and D. Similarly, there were also no significant differences in mechanical strength between groups L and D. Therefore, the decomposition of denture base resin by photocatalysis was not considered to be a dominant factor in the reduction of mechanical strength.

For specimens containing 5% of photocatalyst, their decomposition ability was higher than the non-containing ones and their reduction in mechanical strength was smaller than the specimens containing 10 and 15% of photocatalyst. Based on these results obtained in the present study, the denture base resin containing 5% of photocatalyst seemed to be the most feasible material with self-cleaning ability. However, the mechanical strength of specimens containing 5% of photocatalyst revealed a 35% reduction at 90 days and a 33% reduction at 180 days after polymerization. In clinical use, this reduction in mechanical strength at 90 and 180 days after polymerization is unfavorable and unviable as a denture base material.

To use this material for clinical practice, further investigations with twofold purposes need to be conducted: (1) to determine the effective intensity of ultraviolet irradiation needed to increase decomposition ability; and (2) to determine the polymerization conditions needed to increase mechanical strength in the denture base resin containing 5% of photocatalyst with antimicrobial effects.

ACKNOWLEDGEMENTS

The authors thank Mr. Brian Quinn for his linguistic advice concerning the manuscript.

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