Deterioration of polymethyl methacrylate dentures in the oral cavity

Hirosi MATSUO1,2, Hanako SUENAGA1,3, Masatoshi TAKAHASHI4, Osamu SUZUKI5, Keiichi SASAKI6 and Nobuhiro TAKAHASHI2

1 Division of Advanced Prosthetic Dentistry, Tohoku University Graduate School of Dentistry, 4-1 Seiryo-machi, Aoba-ku, Sendai 981-8575, Japan
2 Division of Oral Ecology and Biochemistry, Tohoku University Graduate School of Dentistry, 4-1 Seiryo-machi, Aoba-ku, Sendai 981-8575, Japan
3 Division of Preventive Dentistry, Tohoku University Graduate School of Dentistry, 4-1 Seiryo-machi, Aoba-ku, Sendai 981-8575, Japan
4 Division of Dental Biomaterials, Tohoku University Graduate School of Dentistry, 4-1 Seiryo-machi, Aoba-ku, Sendai 981-8575, Japan
5 Division of Craniofacial Function Development, Tohoku University Graduate School of Dentistry, 4-1 Seiryo-machi, Aoba-ku, Sendai 981-8575, Japan

Corresponding author, Nobuhiro TAKAHASHI; E-mail: nobu-t@dent.tohoku.ac.jp

Polymethyl methacrylate (PMMA)-made prostheses used in the oral cavity were evaluated by multimodal assessment in order to elucidate the biodeterioration of PMMA. In used dentures (UD), the micro-Vickers hardness of the polished denture surface and denture basal surface was lower than that of the torn surface (p<0.05), whereas the shaved surface approximately 100 µm from the polished surface showed a similar value to the torn surface. By contrast, there were no differences among these surfaces in new resin (NR). The volatile content of UD was higher than that of NR (p<0.05). Component analysis by ATR-FTIR showed specific spectra (1,700–1,400 cm⁻¹) only in UD. This study revealed that PMMA deteriorated during long-term use in the oral cavity in terms of hardness and volatile content with component alteration, and suggests the involvement of biodeterioration, possibly due to saliva and oral microbiota.

Keywords: Biodeterioration, PMMA, Denture, Saliva, Oral microbiota

INTRODUCTION

In dental treatments, biomaterials such as metals and polymers are widely used for recovery and reconstruction of the shape and function of the mouth. Polymethyl methacrylate (PMMA) is frequently applied to the bases of the shape and function of the mouth. Polymethyl methacrylate (PMMA) is deteriorated biologically after long-term clinical use. To test this hypothesis, PMMA-made prostheses used in the oral cavity were evaluated by multimodal assessment, considering the possible biodeterioration of PMMA in the oral cavity.

MATERIALS AND METHODS

Materials

Specimens were collected from 12 pieces of dentures which had been used for 2 to 10 years by patients who consulted the Prosthodontic Clinic, Tohoku University Hospital, Sendai, Japan. To avoid the effect of the type of PMMA products on test results, only dentures made from ACRON MC (GC Co., Ltd, Tokyo, Japan) were selected by checking the dental treatment records or the prescription for the dental laboratory. The dentures were provided by patients who signed a consent form after full explanation of the procedures. After removing debris and denture plaque and taking their dental history regarding the denture, PMMA samples (20 mm in length and width, 2 mm in height) were collected from used dentures (designated as UD) by cutting the dentures using a separating disk (Separate Disk, SHOFU Inc., Kyoto, Japan) and removing the heat-denatured part, that occurred while cutting using the grinding and polishing machine (SCANDIMATIC Universal; SCANDIA, Hagen, Germany) and stored in moist chamber to keep high humidity at a temperature of 3°C until just before tests. One specimen was extracted from each used dentures. Table 1 shows the clinical information of 12 UD. Research protocols were approved by the Research Ethics Committee of Tohoku...
Table 1  Clinical information about used dentures (UD)

<table>
<thead>
<tr>
<th>#</th>
<th>Sex</th>
<th>Age</th>
<th>Duration (years)</th>
<th>Smoothness$^a$</th>
<th>Denture cleaner</th>
<th>Discoloration$^b$</th>
<th>Accretion$^c$</th>
<th>Repair history</th>
<th>Sample site</th>
<th>Other conditions</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>F</td>
<td>67</td>
<td>2</td>
<td>++</td>
<td>use</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
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<td>F</td>
<td>67</td>
<td>2</td>
<td>−</td>
<td>use</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Maxillary bucco-distal border</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>63</td>
<td>3</td>
<td>++</td>
<td>use</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Mandibular linguo-distal border</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>67</td>
<td>3</td>
<td>+</td>
<td>use</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Site of palate</td>
</tr>
<tr>
<td>5</td>
<td>F</td>
<td>63</td>
<td>3</td>
<td>+</td>
<td>no use</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Mandibular lingual border</td>
</tr>
<tr>
<td>6</td>
<td>F</td>
<td>63</td>
<td>3</td>
<td>++</td>
<td>use</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Mandibular bucco-distal border</td>
</tr>
<tr>
<td>7</td>
<td>F</td>
<td>67</td>
<td>3</td>
<td>+</td>
<td>use</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Maxillary buccal border</td>
</tr>
<tr>
<td>8</td>
<td>F</td>
<td>67</td>
<td>3</td>
<td>++</td>
<td>use</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Site of maxillary tuberosity</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>81</td>
<td>8</td>
<td>+</td>
<td>no use</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>Site of retromolar pad</td>
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<tr>
<td>10</td>
<td>F</td>
<td>64</td>
<td>10</td>
<td>−</td>
<td>no use</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>Site of maxillary tuberosity</td>
</tr>
<tr>
<td>11</td>
<td>F</td>
<td>64</td>
<td>10</td>
<td>−</td>
<td>use</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>−</td>
<td>Mandibular linguo-distal border</td>
</tr>
<tr>
<td>12</td>
<td>M</td>
<td>72</td>
<td>10</td>
<td>−</td>
<td>no use</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>Maxillary bucco-distal border</td>
</tr>
</tbody>
</table>

$^a$ Determined by naked eye; ++, very smooth and shiny as new resin; +, smooth; −, cloudy.
$^b$ Determined by naked eye; ++, mostly colored; +, partially colored; −, no colored.
$^c$ Determined by naked eye; ++, mostly covered by debris/plaque; +, partially covered by debris/plaque; −, no debris/plaque.
$^d$ Denture was transferred out of the mouth.

University Graduate School of Dentistry.

Three sets of PMMA plates (20 mm in length and width, 2 mm in height) were prepared as controls using the same type of product (ACRON MC). After polymerization following the instructions, to simulate a polished denture surface and denture basal surface, one side of the plates was polished by using grinding and polishing machine with waterproof abrasive paper (#320, 600, 1000, and 1200, PLANE-0-GRIP, FINEPLANE HERMES Schleifscheiben; SCANDIA) and denture polishing paste (Pika TOP paste D, Pika paste G; Toprer Dental Co., Ltd, Soja, Japan), while the other side was kept intact. Then, the plates were immersed in deionized water for a week to remove residual monomer in PMMA and absorb the maximum water. Finally, the first set of plates was stored at 3°C and 100% humidity until just before tests as a control of new resin (designated as NR). The second set had been kept under the same condition for two years as a control of unused resin (designated as UUR). The third set had been kept in the oral cavity of a healthy volunteer for 2 days as a control of new resin kept in the oral cavity (designated as NRO) The volunteers kept NRO samples without any equipment and removed the samples while sleeping and eating. NRO samples were not cleaned before component analysis. Shaved surfaces (approximately 100 µm from the polished surface for the hardness test, and approximately 100 and 200 µm from the polished surface for component analysis) and the torn surface for the hardness test were also prepared using the grinding and polishing machine.

**Hardness test**

The micro-Vickers hardness of the polished denture surface, denture basal surface and 100-µm shaved surface were measured using a microhardness tester.
(HM-221, Mitutoyo Co., Ltd, Kanagawa, Japan) with 4.9×10^-2 N testing load for 10 s. The torn surface was created by dimidiating the specimens using a separating disk (Separate Disk, SHOFU Inc., Kyoto, Japan) and removing the heat-denatured part, that occurred while dimidiating using the grinding and polishing machine, and analyzed for hardness as comparison criteria. The hardness of 7 points on each surface was measured and average values of 5 points, excluding maximum and minimum values, were calculated.

**Volatile content analysis**
Specimens were weighed using an electric balance (Sartorius, CP 64; Sartorius Co., Ltd, Tokyo, Japan) before and every 24 h after placing specimens in the drying oven (Yamato, SH-41; Yamato Science Co., Ltd, Tokyo, Japan). Measurement was according to the Japanese Industrial Standards (JIS K 7029: 2000), with a minor modification that the minimum unit was changed from 0.2 mg to 0.1 mg because of the light weight of the specimen. Measurement was repeated until the value reached a plateau, and the volatile content was defined as the decrease of weight.

**Component analysis**
Spectra were collected using Attenuated Total Reflection (ATR) Fourier Transform Infrared Spectroscopy (FTIR) (FT/IR 6300; Jasco Co., Ltd, Tokyo, Japan) with an ATR accessory equipped with a crystal prism, in the range of 3,200–600 cm⁻¹, at a resolution of 4 cm⁻¹ and 50 co-added scans. The ATR-FTIR technique is appropriate for the identification of structural changes on the surface of the objects, because the infrared beam penetrates only a few dozen µm into the investigated material. Therefore, since denture plaque or saliva on the surface might affect the spectrum, not only UD, NR and UUR but also NRO were analyzed to confirm the effect. ATR-FTIR analyses were performed on the polished denture surface, and 100-µm and 200-µm shaved surfaces of each specimen. Both torn and basal surfaces were too rough to be applied.

**Statistical analysis**
The differences of the micro-Vickers hardness among the polished denture surface, denture basal surface, 100-µm shaved surface and torn surface within UD, NR or UUD samples were tested using one-way repeated measure analysis of variance (ANOVA) and Dunnett’s test (Dr. SPSS II; SPSS, Chicago, IL, USA) within UD, NR or UUD. The differences of volatile contents among UD, NR and UUD were tested using Student’s t-test (EXCEL; Microsoft Co., WA, USA). Pearson’s correlation coefficient was used to evaluate the relation between the denture condition and the results in the hardness test, volatile content analysis and component analysis.

**RESULTS**

**Hardness test**
Figure 1 shows the relative micro-Vickers hardness of UD, NR and UUR as 100% at torn surface. In UD, the micro-Vickers hardness of the polished denture surface and denture basal surface was significantly lower than that of the torn surface (p<0.05; one-way ANOVA, Dunnett’s test), whereas the 100 µm-shaved surface showed a similar value to the torn surface (Fig. 1a).

Although there was no significant difference in hardness between the polished surface and basal surface in UD, the former tended to show a lower value than the latter. By contrast, there were no differences among these surfaces in NR and UUR (Figs. 1b and 1c).

**Volatile content analysis**
Figure 2 shows the percentage change in weight of UD, NR and UUR. The decrease in weights of NR and UUR stopped within 1 day after placing in the oven, while that of UD continued for 4 days. The ratio of volatile content, defined as the decrement percent in weight, of UD (4.04%) was significantly higher than those of NR (2.48%) and UUR (2.21%) (p<0.05; Student’s t-test). A pungent smell was noted from the drying oven when UD was drying.

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**Fig. 1** Micro-Vickers hardness of (a) used denture (UD), (b) new resin (NR), and (c) unused resin for two years (UUR).

* *p<0.05 one-way ANOVA, Dunnett’s test.*
Component analysis
Figures 3a and 3b display the typically observed ATR-FTIR spectra of UD and NR, respectively. Although UD had a similar pattern to NR in general, several specific spectra were observed in the region of 1,700–1,400 cm\(^{-1}\) only in UD. These specific spectra were observed on the 100-µm shaved surface clearly and also on the polished surface even though some of those spectra were inverted or condensed, but not on 200-µm shaved surface (Fig. 3a). It is likely that the inverted or condensed spectra were induced since the polished surface was not as flat as shaved surface. The specific spectra were confirmed for all 12 specimens of UD. Figure 3b shows magnified spectra in the region of 1,700–1,400 cm\(^{-1}\) of specific spectra. On the other hand, the specific spectrum was not observed on any surface of NR (Fig. 3c). Furthermore, UUR and NRO had nearly identical spectra to NR without the specific spectra observed in UD (Fig. 3d).

Relationship with denture condition
There was no specific relationship between the condition of used dentures (gender and age of denture user or duration of use) and any of the results in the hardness test, volatile content analysis and component analysis.

Fig. 2 Percentage change in weight of used denture (UD), new resin (NR) and unused resin (UUR).

*\(p<0.05\) Student’s t-test.

Fig. 3 ATR-FTIR spectra of PMMA resin.
(a) used denture (UD), (b) magnified spectra of (a) in the region of 1,700–1,400 cm\(^{-1}\), (c) new resin (NR), (d) unused resin (UUR) and new resin kept in the oral cavity (NRO). The spectra of NR are also indicated in (a), (b) and (d) for comparison.


**DISCUSSION**

**Hardness test**

Mechanical strength of resin is usually evaluated by the three-point bending test, compression test, tensile test, impact test, general hardness test (Vickers, Knoop, Mohs and Brinell), and others; however, these tests require a large standardized specimen. Therefore, the micro-Vickers hardness test was adopted in this study to evaluate specimens of used dentures with small and rounded surfaces.

With UD, the significant decreases in the polished and basal surface hardness indicate deterioration caused by exposure to the oral cavity (Fig. 1a). However, no significant change was observed on the 100-µm shaved surface, suggesting that deterioration was limited to the superficial layer. The lack of differences among surfaces in NR and UUR (Figs. 1b and 1c) showed agreement that long-term exposure to the oral cavity can lead to a decrease in hardness of the surface. On the other hand, occlusal force and thermal changes due to food and drink can be transmitted to the dentures (>100 µm), supporting that the decrease in hardness is caused not only by physiochemical factors but also by biological factors such as salivary enzymes and/or oral microbiota.

**Volatile content analysis**

The volatile content ratio of NR (2.48% by weight) and UUD (2.21%) in this study are due to natural water absorbability of PMMA and are nearly consistent with a previous report (2.26%). However, the slow but large reduction of weight (4.04%) with a pungent smell in UD indicates that UD had absorbed a large amount of water and volatile materials such as organic acids, often produced by saliva and microbiota. Flexural fatigue due to the occlusal force during long-term clinical use therefore generates cracks and thus increases porosity. The higher volatile content ratio of UD could be attributed to enhanced penetration of volatiles through increased micro-cracks and porosity. Takeuchi et al. (2012) reported that bacteria were detected in the internal layer of denture bases after long-term use, suggesting that bacteria invaded dentures through micro-cracks and induced biodeterioration by their enzymatic activity and production of volatile metabolites. Thus, although physiochemical factors, such as occlusal force and thermal change, may relate to micro-cracks and increased porosity, it is possible that deterioration was synergistically accelerated by biological factors such as saliva and microbiota in micro-cracks. Additionally, since volatile content of UD was higher than that of UUR, biological factors in the oral cavity might increase the elution amount of monomer during long-term use.

**Component analysis**

Several specific spectra in the region of 1,700–1,400 cm\(^{-1}\) found only in UD suggest that the component of UD surface had been modified during long-term use. No specific spectra observed in NRO (Fig. 3d) indicate that the spectra were not due to organic constituents derived from saliva or microbiota in the oral cavity. It is thought that mechanical stress such as occlusal force and thermal stress such as dietary components affect not only on the surface but also the inside of denture materials. The specific spectra observed only on the polished surface and the 100-µm shaved surface indicates that deterioration was limited to the superficial layer and the spectra were not due to occlusal force or thermal stress. In addition, usage of denture cleaner had no effect on the result of component analysis (Table 1). All these results indicate that only the shallow layer of denture surface was modified structurally during long-term usage, and suggest that PMMA might be deteriorated by salivary enzymes and/or microbial enzymes/metabolites, which might induce chemical reactions underlying the structural modification. However, the mechanism of these reactions is still unknown and further study is clearly needed.

**CONCLUSION**

This study revealed that PMMA deteriorated during long-term use in the oral cavity in terms of hardness and volatile content. Furthermore, component analysis suggested that this deterioration could occur only in the shallow layer of the surface due to the exposure to the oral cavity, where salivary enzymes and/or microbial enzymes/metabolites are involved, that is, biodeterioration. In addition, testing methodologies in this study made it possible to analyze the deterioration of used dentures. These methods will be useful for clinical assessment of denture remanufacture and for development of dental, medical and industrial materials with high resistance to both physiochemical and biological factors.

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