Ultrasound treatment reduced residual monomer in methyl methacrylate-based orthodontic base-plate materials

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Abstract

Objective: To evaluate the effect of ultrasound treatment time on the level of residual monomer (LRM) in methyl methacrylate (MMA)-based orthodontic base-plate materials.

Methods: Forty-eight-disc specimens with a 50-mm diameter and 3-mm thickness fabricated from Orthocryl (OC, Dentaurum) and Orthoplast (OP, Vertex) self-cure acrylic were prepared according to their manufacturers' instructions and ISO 20795-2 (2013). They were randomly divided into eight groups (n=6): Group I, untreated controls; Groups II and III, immersed in room temperature water for 24 and 72 h respectively; Groups IV-VIII immersed in 50°C water in an ultrasonic bath for 3, 5, 10, 15 and 20 min respectively. The LRM was determined using a high-performance liquid chromatography. Data were analyzed by a one-way ANOVA, followed by Tukey's HSD post hoc test (P < 0.05).

Results: The LRM in OC II-VIII groups were significantly lower than those in the OP II-VIII, and were lower than that in the OC I. The LRM in OP III group was lower than that in the OP I. The LRM in OP VI-VIII groups were not significantly different from that in the OP III.

Conclusion: Water immersion at 50°C in an ultrasonic bath for 10–20 min reduced the LRM in MMA-based orthodontic base-plate materials. The results revealed a convenient reduction of the residual monomer within a short period of time in clinical practice.

Introduction

Orthodontic treatment can be with either fixed or removable appliances. Polymethyl methacrylate, acrylic resin has been widely used in the constructions of both active and passive removable orthodontic appliances for many years [1]. Orthodontic appliances are used for newborn patients with cleft lip and palate, space maintenance, tipping teeth, overbite reduction, thumb-sucking deterrence, block movements and retention after active treatment [2-4]. The appliances are used in children, adult and elderly patients. Moreover, the base plate of orthodontic appliance is kept in contact with oral mucosa for a long time during treatment.

For fabrication, two techniques are possible: a doughing technique, in which liquid and powder are mixed together, is widely utilized in prosthodontics. However, a spray-on technique, in which the polymer is saturated by its monomer, is commonly utilized in orthodontics for removable orthodontic appliances [5].

During the polymerization reaction of acrylic resin, not all of the methyl methacrylate (MMA) monomer is converted into polymer; unreacted monomer called residual monomer (RM) is left [6,7]. When the orthodontic base plate contacts saliva and mucosa, RM will be leached from the acrylic resin to the oral environment [8]. The RM has been reported toxicity and allergic reaction [9-12]. Allergy from the RM is varied among patients from a localized hypersensitive reaction to some systemic involvements [9,10,13-16]. In orthodontics, Gonçalves et al reported a 60-year-old woman who had an allergic reaction to the residual MMA after the insertion of a retainer for one month [9]. Consequently, it is desirable to reduce the residual MMA content in acrylic resin to as low a level as possible, prior to insertion in the patient’s mouth.

In orthodontics, it has been recommended that the RM content of autopolymerized acrylic resin could be reduced by immersion in water for 24 h before usage [17]. In prosthodontics, it has been suggested that dentures should be immersed in water at 50°C for 60 min [18]. However, these methods take a long time to reduce the amount of RM. In some clinical situation, an immediate delivery of the removable appliance to the patient is needed, right after the repairing process and the fabricating an obturator to the cleft lip and palate newborn patient. Therefore, reduction of the RM level within a short period of time should be considered.

An ultrasonic bath is widely used for cleaning dental instruments. Several studies have reported the use of ultrasonic baths to extract chemical substances and nutrients in industry, e.g., extracting mangiferin from Mangifera indica leaves, oil from tobacco, and phenolic compounds from sugar cane [19-21]. Ultrasonic treatment has been firstly reported to reduce the RM level of auto-polymerized acrylic resins used in prosthodontics [22]. However, its...
effectiveness in eluting RM from orthodontic acrylic resin has not been investigated.

The aim of this study was to evaluate the level of residual monomer (LRM) in MMA-based orthodontic base-plate materials after water immersion at room temperature and after immersion in an ultrasonic water bath under various treatment times.

Materials and methods
Sample preparations

Forty-eight disc specimens, 3 mm thick x 50 mm diameter, were prepared from each of two brands of MMA-based orthodontic base-plate materials, that is, Orthocryl (OC; Dentaurum, Ispringen, Germany) and Orthoplast (OP; Vertex Dental, Zeist, The Netherlands), by a spray-on technique (Table 1). The powder to liquid ratio was 2.7:1 in each specimen. The specimens were processed in accordance with the manufacturers’ instructions and ISO 20795-2 (2013) [23]. Powder was placed into a stainless steel mold (50±0.1 mm diameter and 3.0±0.1 mm deep) and liquid dripped into the powder. The powder and the liquid were reappled, until the mold was full. The specimens were placed in a pressure cooker for 20 min (0.22 MPa at 45°C for OC; 0.25 MPa at 55°C for OP according to the manufacturers’ instructions), kept in the dark at 23±2°C for 24±5 h, and wet-ground equally on both sides with P500 and P1200-grit silicon carbide papers. The specimens were checked with a digital caliper to ensure a diameter of 50±1 mm and a thickness of 2.0±0.1 mm (Table 1).

Each brand was divided into eight groups, six specimens per group: Group I, untreated controls; Groups II and III immersed in water at room temperature for 24 and 72 h respectively; Groups IV–VIII immersed in water at 50°C in an ultrasonic bath at 40 kHz for 3, 5, 10, 15 and 20 min respectively.

Residual monomer extraction procedure following ISO 20795-2 (2013)

Each specimen disc was first broken into small pieces. Approximately 650 mg of each broken disc pieces were weighed by a digital scale (Sartorius BP110s, Sartorius, Germany) to four decimal places and treated with 10 ml of tetrahydrofuran (Merck KGaA, Darmstadt, Germany) in a 10 ml volumetric flask for each sample solution. The broken pieces from each specimen were distributed into three sample solutions for the pass/fail determination test for RM. The sample solution was agitated by a magnetic stirring apparatus at 25°C for 72±2 h. A 2-ml of the resultant slurry was transferred to a 10 ml volumetric flask and methanol (Merck KGaA, Darmstadt, Germany) added to a total volume of 10 ml and the solution shaken to precipitate the resin. A 5-ml aliquot was centrifuged at 3000 rpm for 15 min, and 3 ml transferred to separate glass tubes. One ml of the supernatant of each sample was determined the monomer concentration by HPLC for the determination of RM. The three solutions per sample were averaged to generate the representative value of each specimen. Therefore, six values were obtained for each experimental group. The data were analyzed with a one-way ANOVA, followed by Tukey’s post hoc test at the 95% confidence level (P < 0.05) by the SPSS 17.0 software program (SPSS Inc., Chicago, IL).

Results

In the present study, we analyzed the LRM in orthodontic base polymers following the ISO method for the determination of RM. The three specimens that were divided into nine solutions were tested for pass/fail determination of RM. The three solutions per sample were averaged to generate the representative value of each specimen. Therefore, six values were obtained for each experimental group. The data were analyzed with a one-way ANOVA, followed by Tukey’s post hoc test at the 95% confidence level (P < 0.05) by the SPSS 17.0 software program (SPSS Inc., Chicago, IL).

The results revealed statistically significant differences in the LRM after the different treatment methods (Table 2). The highest LRM was found in the OC I group, while the OC VIII group showed the lowest LRM.

According to a one-way ANOVA (Table 2), the LRM in OC II–VIII groups were significantly lower than that in the OC I (P < 0.001). The LRM in OC VIII group was significantly lower than those in the OC II and OC III (P = 0.034 and P = 0.011). The LRM in OC VI and OC VII groups were not significantly different from those in the OC II (P = 0.986 and P = 0.209) and OC III (P = 0.999 and P = 0.088), but the LRM in OC VII group was significantly lower than that in the OC VI (P = 0.003).

In the OP groups (Table 2), no significant difference existed between OP I and OP II groups (P = 0.241), but the LRM in OP III group was significantly lower than that in the OP I (P < 0.001). The LRM in OP VI–VIII groups were not significantly different from that in the OP III (P = 0.124, P = 1.000 and P = 0.430).

In the same treatment method, the OC samples had statistically significantly lower LRM than the OP samples (P < 0.001).

Discussion

Among the orthodontic literature, few studies have examined methods of reducing the LRM in orthodontic acrylic base-plate [24-26]...
Other studies have demonstrated that physical properties are improved as polymer chains decrease, resulting in a reduction in physical properties. Secondary chemical bonding forces (van der Waals forces) between the polymer chains can prevent close packing of the polymer chains, leading to a decrease in physical properties. Consequently, the chemical bonding forces can be reduced by further pushing the polymer chains further apart [32]. Consequently, the LRM in acrylic resin is also related to its physical properties.

High performance liquid chromatography, which is a well-established method for the determination of RM in dental acrylic resins [27–29], is non-destructive, enables simultaneous analysis of various substances, and provides correct estimates of the LRM in acrylic resin [30]. The HPLC was thus used in this study to determine the LRM.

The adverse effects of RM are patient allergy and its effect on physical properties of the acrylic. Orthodontic acrylic resins can cause toxic reactions in permanent cultures of fibroblasts and keratinocytes [31]. Moreover, Gonçalves et al reported an allergic reaction to MMA self-curing acrylic resin during an orthodontic treatment in a 60-year-old woman patient, after an orthodontic retainer had been inserted. A localized hypersensitive reaction on the palate, hypersalivation, a bitter taste in the mouth, and difficulty swallowing were reported [9].

The LRM in acrylic resin is also related to its physical properties. Dogan, et al. found a positive correlation between water sorption and RM. The RM can cause voids in acrylic resin, and when it leaches out, water molecules can penetrate the void and act as a plasticizer by pushing the polymer chains further apart [32]. Consequently, the secondary chemical bonding forces (van der Waals forces) between the polymer chains decrease, resulting in a reduction in physical properties. Other studies have demonstrated that physical properties are improved when the LRM is reduced [33,34].

According to ISO 20795-2, the LRM of orthodontic base polymers should not exceed 5 wt% [23]. In this study, each specimen complied with this requirement. Despite the fact that ISO 1567 was mentioned as a reference [35], LRM was limited to 4.5 wt% for self-curing acrylic resins. Harrison and Hugger referred to the British Standard Institute specification for self-curing orthodontic resin, which requires a 3.5 wt% limit for the LRM [36]. However, Gonçalves et al reported an allergic reaction to the self-curing acrylic resin of an orthodontic retainer base plate [9], although the LRM (~0.75 wt%) were below the limits specified in product standards. Therefore, it is desirable to reduce the LRM in acrylic resin to as low a level as possible, prior to insertion into the patient’s mouth.

The LRM in OC were significantly lower than those in OP after the same monomer elution protocol. This may be an influence of the particle size and the polymeric composition of the powder, as well as each brand’s concentration of initiator and accelerator. The particle size of polymer resin influences the amount of monomer remaining in the polymer, and increasing amounts of accelerator in the liquid will tend to decrease the LRM after polymerization [24].

In the OC group, statistical analysis revealed that the LRM after water immersion at room temperature for 24 and 72 h were significantly less than that of the control group. These results were consistent with those reported by Stafford and Brook, in that the RM is lost rapidly in the first 24 h of water immersion [24]. The LRM in the orthodontic resin falls over time by two mechanisms: the continued polymerization of the monomer, and the leaching out of accelerator in the liquid [37].

The LRM in OC IV-VIII groups were significantly lower than that in the OC I (P < 0.001). The LRM after water immersion at 50°C in an ultrasonic bath was reduced, probably because of the microscopic jets of liquid produced by the cavitation. The jets were able to enhance the leaching out of RM from the surface of specimen. Moreover, immersion in hot water (50°C) promoted a more rapid diffusion of RM into water and increased polymerization at the sites of active radicals [27,38].

The LRM of autopolymerized acrylic resins could be reduced by immersion in water for 24 h before usage [17,24], but a prolonged period is needed. On the other hand, immersion in an ultrasonic water bath needs less time to reduce the LRM in orthodontic base-plate materials. Therefore, the LRM in the orthodontic base-plate materials should be reduced by water immersion at 50°C in an ultrasonic bath for 10-20 min before delivery to the patients, when repairing and delivering an orthodontic appliance within a clinical visit.

Ultrasonic treatment with 50°C water may affect the amount of residual monomer in two ways. First, enhanced residual monomer reduction has been attributed to the propagation of ultrasound pressure and cavitation. The implosion of cavitation bubbles generates macro-turbulence, high-velocity inter-particle collisions, and perturbation in acrylic resin micro-pores, which accelerates the eddy diffusion and internal diffusion of monomer [22]. Second, the increased water temperature increased the mobility of the monomer molecules leading to increased number of polymerized polymer chains and may result

### Table 1. Chemical composition of MMA-based orthodontic base-plate materials

<table>
<thead>
<tr>
<th>Brand</th>
<th>Components</th>
<th>Composition</th>
<th>Manufacturer</th>
<th>Batch number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthocryl</td>
<td>Powder</td>
<td>Poly(methyl methacrylate)</td>
<td>Dentaurum, Ispringen, Germany</td>
<td>98210600</td>
</tr>
<tr>
<td>(OC)</td>
<td>Liquid</td>
<td>Methyl methacrylate, methyl acrylate, methyl isobutyrate, ethylene dimethacrylate, 2-(2H-benzotriazol-2-yl)-p-cresol</td>
<td></td>
<td>91839501</td>
</tr>
<tr>
<td>Orthoplast</td>
<td>Powder</td>
<td>Poly(methyl methacrylate) &gt;99%, accelerator &lt;1%, color agents &lt;1%</td>
<td>Vertex, Zeist, The Netherlands</td>
<td>74-957</td>
</tr>
<tr>
<td>(OP)</td>
<td>Liquid</td>
<td>Methyl methacrylate &gt;85%, ethylene glycol dimethacrylate &lt;5%</td>
<td></td>
<td>14003860</td>
</tr>
</tbody>
</table>

### Table 2. Means (wt%) and standard deviations of residual monomer concentration (n = 6)

<table>
<thead>
<tr>
<th>Group</th>
<th>Treatment</th>
<th>Orthocryl (OC) (n=6)</th>
<th>Orthoplast (OP) (n=6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, 25°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Control</td>
<td>3.31±0.18&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.27±0.10&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>II</td>
<td>24 h</td>
<td>2.31±0.13&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>3.06±0.09&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>III</td>
<td>72 h</td>
<td>2.34±0.11&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>2.75±0.04&lt;sup&gt;cd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ultrasonic bath, 50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>3 min</td>
<td>2.70±0.22&lt;sup&gt;e&lt;/sup&gt;</td>
<td>3.08±0.06&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>V</td>
<td>5 min</td>
<td>2.76±0.17&lt;sup&gt;e&lt;/sup&gt;</td>
<td>3.14±0.03&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>VI</td>
<td>10 min</td>
<td>2.42±0.13&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.98±0.10&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>VII</td>
<td>15 min</td>
<td>2.10±0.26&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.73±0.13&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>VIII</td>
<td>20 min</td>
<td>2.04±0.08&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.56±0.08&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Means with the same lowercase letter are not significantly different at P < 0.05 by a one-way ANOVA with Tukey’s HSD post hoc test.
in higher monomer conversion compared with the untreated group. Future studies should focus on the elution of residual monomer into the environment coupled with the comparison of the degree of conversion before and after ultrasonic treatment. The properties of the acrylic resin, determined in ISO 20795-2, should also be investigated.

Conclusions

Using the same monomer elution method, the LRM in OC was lower than that in OP. Water immersion at 50°C in an ultrasonic bath for 10-20 min reduced the LRM in both MMA-based orthodontic base-plate materials, which was similar to or better than water immersion at room temperature for 24 and 72 h. However, less time was required. The results revealed a convenient reduction of the residual monomer within a short period of time in the clinical practice.

Author contribution

Dr. Pajima Thaithammayan participated in the literature search, laboratory work, data collection and manuscript drafting. Assoc. Prof. Chintana Sirichompun contributed to the idea and design of the study protocol, coordinated the research project and revised the manuscript critically for important intellectual content. Assoc. Prof. Chaitarit Wiwatwarrapan contributed to the idea and design of the study protocol, performed the statistical analysis and revised the manuscript critically for important intellectual content. All authors read and approved the final manuscript.

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Conflicts of interest

The authors have no conflicts of interest relevant to this study.

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