



## Influence of Acrylic Resin Polymerization Methods on Residual Monomer Release

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### ABSTRACT

**Aim:** The aim of this study was to quantify and compare the amount of methyl methacrylate (MMA) monomer released from three different denture base acrylic material processed by different polymerization methods and storage conditions.

**Materials and methods:** Microwave-cured, conventional heat and injection-technique acrylic polymerized materials were stored in neutral (pH = 7) and acidic (pH = 4.5) artificial saliva for 24 hours at the room temperature, separately. The residual MMA content was determined by high performance liquid chromatography (HPLC).

**Results:** The MMA leaching from resins showed that microwave-cured material has lower residual MMA leach compared both conventional and injection-technique on neutral saliva storage conditions.

**Conclusion:** The all data's exhibited higher MMA release into an acidic saliva environment than neutral artificial saliva and there were no significant differences between the materials groups on acidic saliva storage conditions.

**Clinical significance:** Microwave polymerization method might has some advantages on reducing release of MMA concentration and may contributory effect upon polymerization reaction on neutral pH storage condition, therefore methods of polymerization should be considered as amount of monomer release.

**Keywords:** MMA, Release, HPLC, Monomer.

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**Conflict of interest:** None declared

### INTRODUCTION

Polymerization of acrylic resins can be processed in different ways and are classified as chemical activation, visible light activation and heating activation which can be generated by using hot water or microwave energy.<sup>1</sup> Despite the various polymerization methods used to initiate the

polymerization of denture base resins, the conversion of monomers to polymers is not complete and some unreacted monomers, called residual monomers, are left in the denture base polymers.<sup>2,3</sup> Allergic reactions to acrylic dentures, either autopolymerized, heat or microwave-polymerized have been described to residual methyl methacrylate (MMA) monomer.<sup>4</sup>

The residual concentration of MMA monomer has been examined widely for many reasons including polymerization conversion efficiency and influences several physical and mechanical properties due to leaching of MMA from resin-based materials. It may also lead to effect mechanical properties such as wear resistance, hardness and susceptibility to discoloration reactions.<sup>5,6</sup> MMA monomer residual concentration is especially dependent upon the efficiency of the polymerization degree and technique.<sup>3,7</sup> If monomer concentration in saliva is highly enough, it may cause irritation, inflammation, hypersensitization and allergic responses of the mucosal tissues.<sup>2,8</sup> Especially children who wear prosthesis and acrylic orthodontic appliances or adults with dentures might be swallowing unknown amounts of MMA for an undetermined period. Therefore, it is necessary to quantify the leach of residual monomers from dental acrylics in different storage conditions.

Many prior studies analyzing the level of residual monomer with different methods such as infrared spectroscopy (IS),<sup>9,10</sup> fourier transform infrared (FTIR),<sup>11,12</sup> gas chromatography (GC)<sup>13,14</sup> and high performance liquid chromatography (HPLC)<sup>2,7,15,16</sup> and recently fluorescent flow injection analysis.<sup>7,17</sup> However, HPLC is widely accepted method for determining MMA in dental acrylic resins.

Recently, curing processes have been modified in order to achieve minimal residual components and improve the physical and mechanical properties of the resin materials,

and also to afford the technical work of the professionals. Different polymerization methods have been used such as conventional heat, light and microwave energy.<sup>9,11</sup> In the conventional heat method, the monomer molecules are inducted by thermic shocks and their movements are only the consequence of the outside heat.<sup>2</sup> In the microwave irradiation method, the monomer molecules are positively moved by a high frequency electromagnetic field and their movements are the cause of the internal heat.<sup>18</sup> As temperature increases, mobility of molecules speeds up and this allows a relatively low processing temperature around the material, resulting in reduced monomer release and a good accuracy.<sup>19</sup> This method also has some advantages such as polymerization time control, homogeneity of the mixture, low release of residual monomer and the achievement of a prosthetic material with excellent adaptation in the clinic works.<sup>1,11,19</sup> Thirdly, an injection method allows directional control of the polymerization process through the flask design. A constant flow of new material from the sprue compensates for the polymerization shrinkage and produces a more accurate denture compared to that produced by the compression molding method.<sup>2,20</sup>

It is well known that a polymerization of several hours at the highest possible temperature and subsequent storage of the denture or orthodontic device for 24 hours in water will minimize the concentration of residual monomers.<sup>21</sup> As there is limited information in the dental literature concerning the evaluation of different storage condition for first 24 hours, the present study aimed to assess the residual MMA leaching from the acrylic resin materials subsequent to storage in different conditions.

## MATERIALS AND METHODS

### Materials

The materials and compositions used in this study are presented in the Table 1. Three different curing methods (heat curing, microwave curing and injection) were used for the investigation. Each experimental group (heat curing; G1, microwave curing; G2, injection technique; G3) consisted of 20 samples (n = 20). Samples were prepared in disk form. Stainless steel I disks with diameter of 65 mm

and height of 40 mm were used to manufacture the wax patterns. The wax patterns were flaked in type II dental stone (Moldano, Bayer, Leverkusen, Germany) using the appropriate flask for curing method. Conventional metal flasks and fiber-glass reinforced plastic flasks (GC, Dental Industry Corp. Tokyo, Japan) were used for heat curing and microwave curing, respectively. For injection molding the special thermal flasks (SR Ivocap Vivadent, Liechtenstein, Germany) were used. The flasks were allowed to set. After the plaster set completely, the conventional metal flasks were boiled for 10 minutes to eliminate the wax. In G2, the flask was preheated in hot water (80°C) for 5 minutes. The wax was removed and the molds were washed out with boiling water. In G3, the wax was softened after the plaster was set and removed in one piece. The residual wax was thoroughly flushed with boiling water. All molds were washed with water and neutral detergent in each flask.

### Sample Preparation and Storage

For all samples, the mixing ratios and methods of preparation were performed according to the manufacturer's instructions.

#### G1 (Conventional Heat Polymerization)

A recommended mixing ratio of 22.5 gm polymer: 10 ml monomer was used for sample preparation with conventional heat-polymerized acrylic resin (Paladent, Heraeus Kulzer GmbH, Hanau, Germany). The polymer and monomer was mixed thoroughly. Subsequently the mixture was left to mature in the closed mixing cup at room temperature for 10 minutes. When the mixture had matured, sufficient amount of dough resin was placed in the cavities and the flask was closed, loaded with 80 bar pressure and fixed with a clamp. Subsequently the flask was placed in cold water, heated up to 100°C and boiled for 45 minutes. After the polymerization process was completed, the flask was allowed to cool down.

#### G2 (Microwave Curing)

The standard powder/liquid ratio of 100 gm powder to 43 ml liquid was used in fabrication of the samples. Required amount of liquid was placed in microwave-cured acrylic

**Table 1:** Composition of the acrylic materials tested in the study

Material name	Company	Processing method	Major chemical compounds
Paladent	Heraeus Kulzer GmbH, Hanau, Germany	Heat polymerization	Powder: Methylmethacrylate copolymer; liquid: MMA, dimethacrylate
Acron™ MC	GC Corp., Tokyo, Japan	Microwave polymerization	Powder: Polymethylmethacrylate, ethylacrylate copolymer; liquid: MMA, N-dimethyl p-toluidine
SR Ivocap Plus	Ivoclar Vivadent, Inc., Liechtenstein, Germany	Injection polymerization	Powder: Polymethylmethacrylate, copolymer and catalyst, liquid: mixture of MMA stab, dimethacrylate and copolymer

resin (Acron™ MC, GC Corp. Tokyo, Japan) mixing jar and subsequently corresponding amount of powder was placed over the liquid. The lid of the mixing jar was closed and left for 20 minutes at room temperature until the dough stage was reached. Then the dough was removed from mixing jar and packed into the flask stored at room temperature. Acron MC was cured with microwave irradiation for 3 minutes at 500 W high frequency 2,450 MHz with a rotating turntable system (Vestel Goldstar ER 535 MT, Manisa, Turkey). Before deflasking, flask was cooled down for 40 minutes at room temperature, and then placed in cold water for complete cooling for 20 minutes.

### G3 (Injection Technique)

The standard capsule containing 20 gm polymer and 30 ml monomer of SR Ivocap Plus (Ivoclar Vivadent Inc, Liechtenstein, Germany) was used in the study. The monomer was poured into the capsule and mixed in the cap vibrator for 5 minutes. Then, the flask was completely inserted into the clamping frame. 6000 Lbs pressure was applied to the clamping frame with flask in a hydraulic press (80 bar). The material was pressed into the mold with an air pressure of 6 bar and the flask remained on the injection unit for 5 minutes. Then the SR Ivocap assembly was placed in polymerization bath. The temperature of the water bath was set in such a way that the water boiled during the entire period. The polymerization period (begins with the boiling of water) was 35 minutes. After the polymerization period was ended, SR Ivocap assembly was removed from the boiling water and immediately placed in cold water. After 20 minutes the pressure apparatus was removed but clamping frame together with flask remained in cold water for an additional 10 minutes.

Following deflasking, samples in each group were randomly assigned and subgroups were made; totally 6 subgroups (n = 10). Samples were immediately put into glass tubes either filled completely with synthetic saliva with neutral (pH = 7) or acidic pH (pH = 4.5). Then tubes were then covered with lid and all samples were stored at 37°C for 24 hours.

### Synthetic Saliva Preparation

The artificial saliva solution was prepared according to Shannon's (1982) method using the following salt proportions: (NaCl: 1.280 gm/l; MgCl<sub>2</sub>(6H<sub>2</sub>O): 0.125 gm/l; KCl: 0.095 gm/l; CH<sub>3</sub>COOK: 1.508 gm/l; CaCl<sub>2</sub>: 0.167 gm/l; K<sub>3</sub>PO<sub>4</sub>(3H<sub>2</sub>O): 0.386 gm/l; H<sub>3</sub>PO<sub>4</sub>: 0.05 ml/l. pH was adjusted to 7 and 4.5 with changing the amount of HCl in distilled water. After storage time, the specimens were removed from the storage medium and analyzed in HPLC calibrated for MMA monomer extract.<sup>22</sup>

### Measurement of Residual MMA Amount by HPLC Analysis

For quantification of the residual MMA contents in the polymerized acrylic specimens were determined with HPLC system. The analysis was performed by HPLC with an HPLC pump (PerkinElmer Series 200 Pump) with a reversed phase stainless steel C18 analytical column (250 × 4 mm with 5 μm Hypersil PEP 300) at room temperature. The mobile phase was methanol and H<sub>2</sub>O (60:40) at a flow rate of 0.8 ml/min and detection was performed at a wavelength of 205 nm. The injection volume was 20 μl loop. Stock MMA standard solutions were prepared from 99% pure MMA. Known concentrations of MMA (Sigma, 250 ml, Lot 122K3755), were run as reference standards.

Triple injections were made for standard of MMA and specimens' solutions. The linear fittings of the calibration curves were calculated for the chromatographic peaks at the corresponding retention time vs monomer concentration. Chromatograms' corresponding to the injection of acrylic samples of MMA is shown in Figure 1. The relationship of MMA concentration with absorbance was plotted using areas under the peak calculated in ppm with retention time 6.7 minutes.

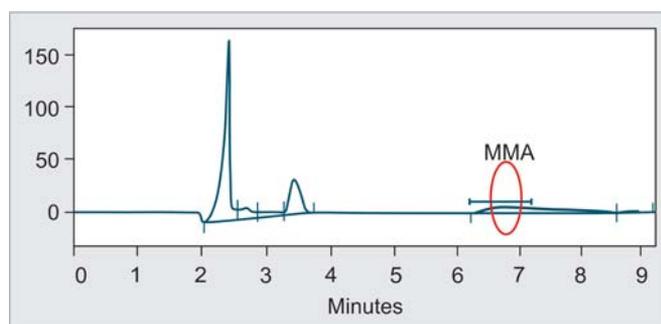
### Statistical Analysis

The mean and standard deviation (SD) for each group was calculated. The findings were analyzed statistically by Kruskal-Wallis test to detect any intergroup differences and

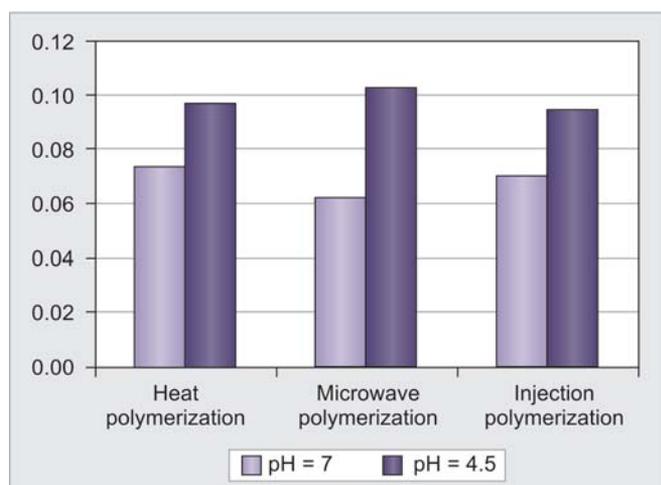
**Table 2:** Mean MMA release (ppm) of acrylic materials and intergroup comparison of difference

	pH 7		pH 4,5		MW	**p
	Mean ± SD	Median (IQR)	Mean ± SD	Median (IQR)		
Heat polymerization	0.074 ± 0.005	0.073 (0.07-0.079)	0.097 ± 0.061	0.093 (0.072-0.105)	17.5	0.142
Microwave polymerization	0.062 ± 0.011	0.064 (0.052-0.072)	0.103 ± 0.074	0.069 (0.066-0.157)	5.5	0.151
Injection polymerization	0.07 ± 0.026	0.074 (0.045-0.079)	0.095 ± 0.004	0.095 (0.094-0.097)	8	0.01*
KW	1.99	3.16				
*p	0.368	0.205				

\*Kruskal-Wallis test; \*\*Mann-Whitney U test; \*p < 0.05



**Fig. 1:** HPLC chromatogram for concentration of MMA leached from acrylic samples with retention time



**Fig. 2:** Mean monomer release (ppm) of acrylic resin materials stored in different artificial saliva conditions

Mann-Whitney U test to evaluate subgroups comparisons at a 5% level of significance.

## RESULTS

Residual MMA amount released into neutral and acidic artificial saliva was determined for three different materials. Figure 2 shows the mean MMA leaching and SD obtained in the groups. Table 2 shows the mean MMA release for groups of heat, microwave and injection polymerization for neutral pH (pH = 7) and acidic pH (pH = 4.5).

The results of the Kruskal-Wallis analysis of variance test exhibited no significant differences ( $p > 0.05$ ) in monomer release among three tested group for neutral and acidic pH in separately. However, all data's exhibited higher MMA release into an acidic saliva environment than neutral artificial saliva. Among the material groups, lower residual MMA monomers obtained leaching from Acron MC specimens compared with Ivocap and Paladent groups on both storage conditions. For Ivocap, statistically higher amount leach was seen on acidic pH saliva conditions compared to neutral pH ( $p = 0.01$ ) Mann-Whitney U test revealed no other significant differences ( $p > 0.05$ ) between the other groups.

## DISCUSSION

Although, acrylic resin materials is widely used in dentistry the elution of components, residual monomers and degradation products from resin materials has a potential impact both on the biocompatibility and the properties of the materials.<sup>6,23</sup> It has been known that monomer conversion is never complete and the degree of conversion varies between 35 and 77%.<sup>6,24,25</sup> A significant amount of residual monomer or short chain polymer remains and can be leached into aqueous media.<sup>25</sup> The degree of conversion also depends on the type and duration of the polymerization and some properties of the dental material such as depth and diameter of dental material.<sup>26</sup> Tuna et al, recently reported that higher monomer release could be determined as the surface area and the storage times are increased; and light curing types and intensity could affect on monomer release.<sup>16</sup>

Attempts have been made to reduce the residual monomer content of acrylic resins by using thermoplastic and microwave polymerization rather than heat polymerization.<sup>13,27</sup> An increase in polymerization temperature and time was accompanied by a decrease in residual monomer content.<sup>13</sup> The use of microwave energy for polymerizing acrylic resins has been also encouraged as a result of less laboratory equipment, the cleanness of the method and the acceptable mechanic properties of the dental material.

The most residual monomers and other compounds are released from the denture base within the first a few days<sup>17</sup> especially during the first days of use and leaching reduce through into saliva or water within following days with much lower rate.<sup>2,15,28</sup> Çelebi et al<sup>2</sup> reported that significant residual MMA leaching occurred within the first 48 hours of immersion for tested resin samples in water followed by gradual longer lasting moderate increase until the 15 days interval. Tsuchiya et al<sup>17</sup> showed that preleaching in water reduced subsequent leaching of MMA, and the amount of reduction depended on an increase in the preleaching temperatures. They recommend that immersion of acrylic resin in hot water (50°C) before insertion especially for autopolymerized resins used either for rebasing or as denture base materials, to minimize the risk of adverse reactions in patients who wear acrylic resin dentures. Vallittu et al,<sup>28</sup> also concluded that if the specimens were immersed in water at 37°C for 24 hours, considerably more monomer was removed than during immersion in water at 22°C. The authors suggested the water immersion of denture in water at 37°C for 1 day prior to insertion.

Taken together, studies addressing residual monomer content and leachable substances from acrylic resins have shown that fairly high amount of substances especially

MMA, may leach into the oral cavity during the initial days after polymerization. It is known that leach of residual monomers and additives from the resin materials should be minimize. Therefore, it's recommended that prosthesis and orthodontic appliances are stored in aqueous media before insertion for a long period of time.<sup>21</sup> The present study results showing the higher residual MMA monomer release from the acrylic samples which stored in artificial saliva with acidic pH for the first 24 hours. It might be desired properties due to after polymerization monomer level highly leached during the first 24 hours and decreased overtime. The lowest residual MMA leach of microwave-polymerized specimens, compared with conventionally heat-polymerized and injection-polymerized technique, are in agreement with the results of some other studies.<sup>2,15,18</sup>

In most studies, release of monomers from polymerized resinous materials has been measured as the total release after a certain period of time.<sup>23</sup> Due to a limited solubility of many of the monomers in water, not all the leachable amount of monomers is accounted when the leaching medium is water.<sup>5</sup> Leaching of monomers from a polymeric material in the mouth might be higher than that measured in water,<sup>29</sup> due to enzymatic breakdown of the monomer which increases the rate of diffusion. However, all *in vitro* experiments, chemicals at the initial stage are changing during the entire course of immersion tests. Previously and currently leached species could be accumulated to change the original chemistry of tested saliva solutions. In this study polymerized acrylic samples were kept in artificial saliva in order to simulate the mouth environment.

## CONCLUSION

Since residual MMA leached from dental base resin materials has adverse effects and allergic reactions on oral tissues, methods to decrease the amount of released compounds in clinical use should be considered. It has been demonstrated that the residual monomer content could be lowered if the denture was stored in water after processing. During this retention time storage conditions might influence the result of the amount of MMA. Regarding the findings of this study, acidic artificial saliva seems better alternative for storage than neutral artificial saliva condition for acrylic resin-based materials especially for the first 24 hours immersion.

## CLINICAL SIGNIFICANCE

The present study demonstrated that microwave polymerization method might has some advantages on reducing release of MMA concentration and may contributory effect upon polymerization reaction. In

addition, it was displayed that acidic saliva conditions has released more monomer than neutral saliva conditions. Due to, most residual compounds release occurred from the resin-based materials within first 24 hours after polymerization, it seems microwave irradiation and storage acrylic appliance in acidic saliva for 24 hours could be advantageous effect on amount of monomer release.

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