

Using of HPLC Analysis for Evaluation of Residual Monomer Content in Denture Base Material and Their Effect on Mechanical Properties

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Abstract: *The samples were prepared according to the routine work for sample preparation in dental laboratories. After reaching dough stage, the mixture packed into dumbbell shaped of stainless steel mould and pressed in a hydraulic bench press for 25 min at room temperature. For heat-cure, the polymerization cycle was carried out using water bath, while self-cure done at room temperature. The residual monomer content was evaluated using high performance liquid chromatography (HPLC). The tensile test was evaluated in dry and wet condition (distilled water). The results showed that the residual monomer content for heat-cure samples was 1.44 wt. % while self-cure samples was 8.71 wt. %. The residual monomer content of heat-cure samples was comply with ISO-1567 standard for denture base material. The heat-cure material depicted higher tensile strength, tensile strain and energy at break than that of self-cure material. This is due to higher residual monomer content in self-cure which acts as plasticizer, subsequently lead to reduce the properties of self-cure material. After immersion, the tensile strength, tensile strain and energy at break of heat-cure samples found to decrease, while the self-cure samples were found to increase. Generally, the heat-cure material showed better properties compared to self-cure material.*

Keywords: residual monomer, mechanical properties, denture base materials

1. INTRODUCTION

Poly (methyl methacrylate) (PMMA) is currently the material of choice for denture base fabrication. The denture base resin is subjected to various stresses during function. During fabrication of a denture, the physical and mechanical properties influence by cure condition and choice of materials. Each cure cycle or fabrication technique is a compromise that attempts to optimize the properties thought important for a given application. Dentists and manufacturers of denture base materials have long been searching for ideal materials and designs for dentures. So far, the results have been noteworthy although there are still some physical and mechanical problems with these materials.

During clinical use, the denture base materials are immersed in saliva and when not in use may be soaked in water. When immersed in such solutions,

plasticizers and other soluble components may leach out over extended periods, while water or saliva is absorbed. The loss of plasticizer may cause brittleness and increased hardness values. Several investigators have evaluated the effect of water on the bond strength of acrylic materials and demonstrated that absorbed water can have a detrimental effect on bond strength to acrylic resin. Furthermore, Dootz et al.¹ have shown that material aging can dramatically affect the physical and mechanical properties.

Sanders et al.² compared acrylic resin record bases made from three commercial resins processed by water bath curing and microwave curing energy. The adaptation of the record bases to a standard cast was measured to determine if there were any statistical significant differences in the fit that could be attributed to the differences in curing methods and the brands of resin. The results indicated a small statistically significant difference in favor of the water bath cure but clinically there were no appreciable differences in the adaptation of the record bases with either curing method or the resins used. The adaptation of artificial dentures made from acrylic resins is clinically acceptable with either microwave curing or the water bath method. Lai et al.³ compared between the conventional method (water bath heat-cure) and microwave method, where materials were tested for hardness, porosity, flexural properties, solubility and molecular weight. They found no difference in the mean values of surface hardness and the weight percentages of the insoluble parts. The mean domain size and the volume fraction of the rubber phase favor that of the water-bath cured specimens.

Naik and Jabade⁴ evaluated and compared the transverse and impact strength of a new high-impact denture base resin with the two most commonly available resins in the market. The materials used were DPI-TUFF, Lucitone 199 and DPI heat-cure denture base resins. They found that the use of long polymerization cycle increases the transverse and impact strength values of these materials as compared to the use of short polymerization cycle.

In the present study, the residual monomer content was evaluated by HPLC, and mechanical properties of heat-cure and self-cure denture base materials were checked out in both dry and wet condition using distilled water.

2. EXPERIMENTAL

2.1 Materials

Two denture base materials that were commercially available, heat-cure and self-cure were supplied by Meliodent-Germany in the form of powder and liquid. The powder contains approximately 97% PMMA polymer while the liquid

is methyl methacrylate monomer mixed with dimethacrylate as the cross-linking agent.

2.2 Specimen Preparation

2.2.1 Heat-cure denture base material

Specimens of heat-cure polymerized denture base were prepared as recommended by the manufacturer and the daily routine work for sample preparation in dental laboratory was followed. The recommended mixing ratio for heat-cure was 35 g powder to 14 ml liquid. The required amount of liquid poured into a mixing jar, then the powder was added carefully until the powder completely wetted by liquid. After reaching dough stage, the mixture packed into dumbbell shaped stainless steel mould. A thin layer of polyethylene sheet was used as the separating media. It was then pressed in a hydraulic bench press for 25 min at room temperature. The polymerization cycle that carried out using water bath at boiling temperature was then switched off and left for 15 min. It was then boiled again for 20 min and then switched off let it to cool down slowly. Specimen was taken out from mould and the excess margins were polished by the sandpaper.

2.2.2 Self-cure denture base material

The recommended mixing ratio was 10 g powder to 7 ml liquid. The required amount of liquid poured into a mixing jar, and with the corresponding amount of powder added, it was mixed thoroughly for approximately 30 s. After reaching dough stage, the mixture packed into dumbbell shaped of stainless steel mould, and with a thin layer of polyethylene sheet used as the separating media, it was pressed under a pressure of 2 pars. The processing and hardening time at room temperature were approximately 2 min and 10–14 min, respectively.

2.2.3 Determination of residual monomer in the denture base materials using HPLC

HPLC was used to quantity the residual methyl methacrylate (MMA) content in the sample of heat-cure and self-cure material. A sample of 50 mg was dissolved in 1 ml of acetone and then 10 ml of methanol was added to the solution to precipitate the polymer. The supernatant of solution was filtered through a 0.45 μm pore Millipore filter. HPLC analysis was performed using LC-2010C Shimadzu Japan system equipped with a CAPCELL PAK C18 column. Ten ml of the sample solution was injected and analyzed at 40°C at a flow rate of 1.0 ml min⁻¹ with acetonitrile water (50/50). This procedure previously described

by Ohyama and Imai.⁵ The calculation content of MMA (x) in 1 g was calculated using the following formula:

$$(\text{MMA}) X = (P_{vz} \times nst \times Cst \times 20) / (Pst \times nvz) \quad (1)$$

Where,

P_{vz} = Average of injected area, nst = weight of standard sample, Cst = purity of sample, Pst = Average weight of standard sample, and nvz = sample weight.

2.2.4 Tensile tests

Tensile tests were carried out according to ASTM D-638 types IV using electromechanical tensile testing machine (TIRA testing machine, 2850-S 50 KN, Germany). The gauge length was set at 50 mm and crosshead speed at 5 mm min⁻¹. At least five samples were tested for each formulation. Tensile strength, energy at break as well as tensile strain were recorded.

2.2.5 Effect of aqueous environmental on tensile properties

The tensile samples were immersed in distilled water and at room temperature. They were tested at intervals of 1, 7 and 30 days. The specimen's outer surfaces were then manually dried with soft tissue paper. The tensile test was then applied according to the procedures described in previous section.

3. RESULTS AND DISCUSSION

3.1 Residual Monomer Test (HPLC)

Figures 1 and 2 show the diagram of residual MMA collected from 1 g sample of PMMA for heat-cure and self-cure denture base materials, respectively. The content of MMA was calculated from the area under the peak after 6 min from injection of the sample as shown in the diagram. The average of 12 readings of each sample of heat-cure and self-cure denture base materials were shown in Table 1. The results of MMA content were 23.28 mg g⁻¹ (1.44 wt. %) and 140.02 mg g⁻¹ (8.71 wt. %) of heat and self-cure, respectively. It can be seen that the residual monomer content of heat-cure samples was lower than that of the self-cure as well as the ISO-1567 (2000) standard for denture base material. In this study, the curing types (heat-cure and self-cure) have a great influence in reducing the residual monomer content which is in agreement with many researches who reported similar findings.⁵⁻⁷ Significant difference was found in

both heat-cure and self-cure denture base materials in terms of residual monomer content. The self-cure contained residual MMA of 8.71 wt. % which failed to comply with the requirements of ISO 1567 Standard, while the heat-cure passed the requirements regarding residual MMA.

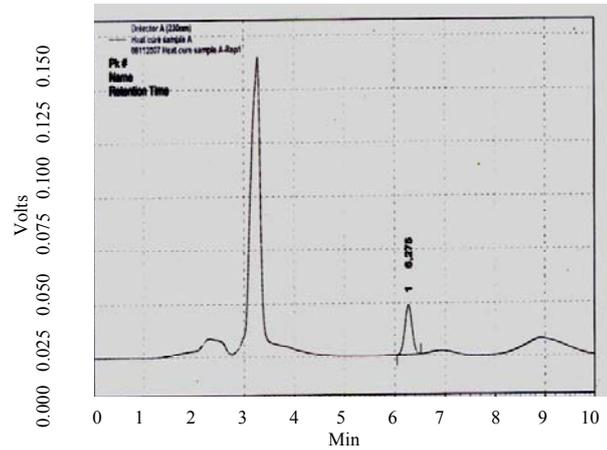


Figure 1: Residual MMA diagram collected from 1 g sample of PMMA for heat-cure denture base material.

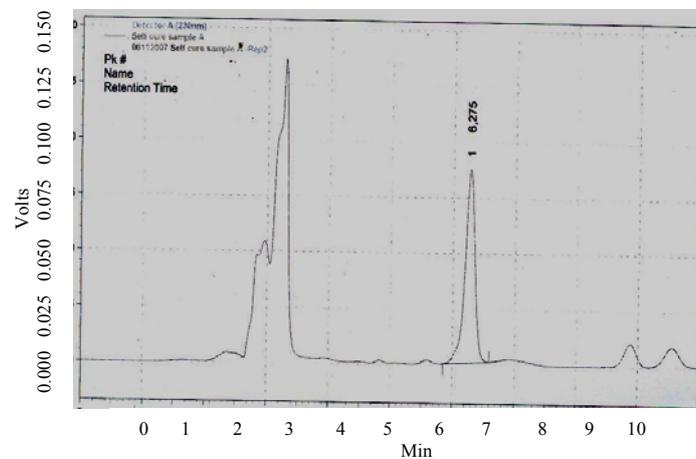


Figure 2: Residual MMA diagram collected from 1 g sample of PMMA for self-cure denture base material.

Table 1: The results of MMA content of denture base materials compared with ISO standard.

Denture base material	Heat-cure	Self-cure	ISO -1567
wt. %	1.44	8.71	2.2
mass	23.28	140.02	35.37

Miettinen and Vallittu⁸ compared the residual monomer content released from heat-cure and self-cure denture base materials and concluded that the self-cure materials released considerably more residual MMA than the heat-cure materials (1–2 wt. %). Moreover, the authors showed that the residual monomer content could be reduced when the polymerization time was extended. Dogan et al.⁹ studied the effects of varying polymerization times and temperatures on the residual monomer content of polymer/monomer-based denture base materials. The authors showed that increased temperatures and extended polymerization time were accompanied by a decrease in the residual monomer content.

3.2 Tensile Properties

3.2.1 Tensile properties at room temperature (dry condition)

Table 2 shows the results of tensile properties of heat-cure and self-cure denture base materials. It can be seen that the heat-cure samples displayed higher tensile properties. The tensile strength of heat-cure was higher by 15.46% than that of self-cure. While the tensile strain was higher by 12.14%, the energy at break also showed higher value by 6.48%. This is due to the higher amount of residual monomer content in self-cure samples (Table 1), which act as plasticizer and give dramatically lower strength. However, tensile modulus of heat-cure was lower by 6.25% which indicated that the self-cure samples were stiffer and less flexible than the heat-cure samples. The results of current study in agreement with other researchers who found that water bath polymerization results in enhanced mechanical properties.^{6,7,10} In addition, Dogan et al.⁹ evaluated the tensile properties of denture base material related to the effect of level of residual monomer, and concluded that the percentage of higher levels of residual monomer effected on the tensile properties of denture base material.

Table 2: Results of tensile properties of heat-cure and self-cure denture base materials at room temperature.

Sample	Tensile strength (MPa)	Tensile strain (%)	Energy at break (N m ⁻²)	Tensile modulus (GPa)
Heat-cure	70.13	6.26	3.24	1.20
Self-cure	59.29	5.50	3.03	1.28

3.2.2 Effect of aqueous environments on tensile properties

The effects of distilled water on tensile properties of denture base materials are shown in Table 3. Heat-cure and self-cure denture base materials were significantly different in their tensile strength. After immersion in the water, the tensile strength was found to decrease due to the absorption of water which acts as plasticizer. The heat-cure sample decreased by 18.11% after 30 days compared to one day immersion. While tensile strain dropped by 19.08%, at the same time, energy at break was lower by 12.14%. This may be attributed to the presence of water in the polymer acting as an internal plasticizer which increases the plasticity as reported by Deb et al.¹¹

The tensile strength of self-cure sample was found to increase after immersion from one day to 30 days. Tensile strength increased by 11.24% while tensile strain, energy at break and tensile modulus found to decrease. After immersion in the water, the residual monomer content can leach out and the water replace them. However, once the majority of the leachable components are extracted.

During storage in an aqueous environment, two processes were occurred simultaneously. First, post-curing of the denture base and leaching of the residual monomer where both effects reduced the amount of monomer in the denture base. The second was water uptake. The changes observed in tensile strength may be due to the water which actually not reducing the strength of the bonds within the PMMA, but allowing the chains to slip over each other more easily. Thus, reducing the stiffness and increasing the ability of the matrix to extend prior to failure. The tensile strain and energy at break showed similar trends to that of tensile strength, with a decrease in stiffness and increase in ductility after a period of immersion in distilled water.

After analyzing the results obtained in the present study, the tensile properties of heat-cure were better compared to self-cure denture base materials. Tsuchiya et al.¹² demonstrated that the residual monomer content of denture base materials is lowered to a quarter of the initial value if the denture is immersed in water at 50°C for one hour after polymerization.

Table 3: The result of the tensile properties of denture base materials after immersed in distilled water.

Sample	Tensile strength (MPa)	Tensile strain (%)	Energy at break (N m^{-2})	Tensile modulus (GPa)
Heat-cure 1 day	70.05	6.76	3.13	1.21
Self-cure 1 day	51.78	5.64	2.9	1.03
Heat-cure 7 days	60.04	5.34	2.76	1.20
Self-cure 7 days	56.96	4.99	2.69	1.11
Heat-cure 30 days	57.36	5.47	2.75	1.22
Self-cure 30 days	58.34	4.45	2.39	1.23

4. CONCLUSION

Heat-cure denture base material exhibited significantly lower residual monomer content than that of self-cure material. In addition, heat-cure material was passed the requirements regarding residual monomer content, while self-cure failed to comply with the requirements of ISO-1567 standard for denture base materials. Heat-cure denture base material exhibited higher tensile strength as compared to self-cure denture base material. Due to the increased concern for quality control and to obtain assured results repeatedly, the evaluation of such newly introduced and currently available products is imperative.

5. ACKNOWLEDGEMENT

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