

# Quantitative Evaluation Of Residual Monomer In Commercially Available Heat Activated Acrylic Denture Base Materials Subjected To Different Curing Regimens

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## ABSTRACT

**Statement of Problem:** Poly(Methyl Methacrylate) resin material that shows evidence of least residual monomer content on processing, should be recommended for clinical usage in order to make it biocompatible and to obtain preeminent physical and mechanical properties.

**Aim:** To quantify the residual monomer in four commercially available heat activated acrylic resin denture base materials cured by different curing cycles.

**Methods:** Four commercially available heat activated acrylic denture base materials viz., Trevalon, Trevalon Hi, Acralyn-H and DPI, were manipulated as per the manufacturer's instructions and were cured using two different curing cycles short (S) and long (L) cycle. After the curing, shavings of the cured acrylic samples were obtained by grinding the samples using carbide bur at a slow speed of 200rpm. Accurately weighed shavings were transferred to a vial containing 10 ml of methanol and stirred to extract residual monomer. The content of residual monomer in methanol was estimated at three different time intervals (immediate, one day and one week) using a High-Performance Liquid Chromatography (HPLC) method.

**Results:** Residual monomer levels were found to be less when the samples were cured using short curing cycle (~1.7%) compared to those cured using long curing cycle (~2.1%). Immersion in water resulted in a substantial reduction in the residual monomer content and this reduction was found to be time dependent.

**Conclusion:** From the results of the present study, it can be concluded that all the selected denture base materials showed minor quantities of residual monomer irrespective of the curing method. Curing cycle involving terminal boil had significant effect in reducing the content. Further, immersion in water for one day significantly reduced the residual monomer content.

**Keywords:** Methyl methacrylate, Residual monomer, HPLC method, Curing cycle

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**Conflict of interest:** None

## INTRODUCTION

Poly(Methyl Methacrylate) (PMMA) has diverse applications in the field of dentistry and medicine. The Heat activated PMMA (H-PMMA) has been a boon to dentistry particularly in the fabrication of removable prosthesis since 1937 when it was introduced by Dr. Walter Wright. [1]. with the introduction of the compression molding technique, the acrylic denture base materials have almost entirely supplanted other materials for denture fabrication [2].

H-PMMA materials are generally supplied as polymer powder and monomer liquid. The polymer and monomer

are mixed in intended proportions to form a dough, which is then compression molded and subjected to heat curing cycle to allow methyl methacrylate to polymerize into poly(methyl methacrylate). However, due to incomplete polymerization, residual monomer may remain in the final cured prosthesis and may result in biological reactions. Though, the toxicity of MMA monomer is not appropriately substantiated [3], allergic reactions to acrylic resins continue to be a great concern and are manifested as delayed or contact type of hypersensitivity. (Stomatitis venenata)[4].The unreacted residual monomer in acrylic

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dentures is usually unavoidable and posed a serious challenge for patients, dentists and the dental technician. Lack of awareness among the dentists and dental technicians on various ways to reduce this unreacted residual monomer from the commonly used heat cure products is the basis for this article.

A number of constituents of this resin, in both its un-polymerized and polymerized state, have been implicated as putative allergens. These include the residual methyl methacrylate monomer (R-MMA), benzoyl peroxide, hydroquinone, formaldehyde and plasticizing agents [5][6]. Among these, R-MMA was the most probable primary irritant and sensitizer as reported by Turrell [7] and Leggat PA [3]. The onset of allergic reactions is more rapid on the mucosa [8], but several other body systems are also affected including skin, respiratory tract, and neurological system [9].

Commercially, several acrylic resins are available claiming superior quality in terms of physical and mechanical properties. However, the basic differences lie principally in particle size, shape, molecular weight, and composition which directly affect the extent of polymerization and the properties of polymerized resin. In addition to the reported biological concerns, R-MMA was found to have significant

effect on physical and mechanical properties of the cured denture bases. Therefore, the primary knowledge of the R-MMA is a prerequisite for corroborating it as an allergen and for the evaluation of properties of the material [2]. In this regard, it is essential to evaluate the commercially available denture base materials for residual monomer concentration to ascertain their potential to cause allergy in patients. Though, Infrared spectroscopy and gas chromatography can be used to determine the residual monomer, they are expensive and cannot be used in a general laboratory set up. High Performance Liquid Chromatography (HPLC), on the other hand, has been widely employed for separation, identification and quantification of variety of molecules in analytical chemistry [8]. It has been widely used to estimate the residual monomer concentration in the denture base materials previously [10] [11].

The aim of the present study is to estimate the R-MMA in four different commercially available heat cure acrylic resin products after subjecting them to different curing cycles using a specifically developed and validated HPLC method.

**MATERIAL AND METHODS**

The detailed material description is shown in table 1

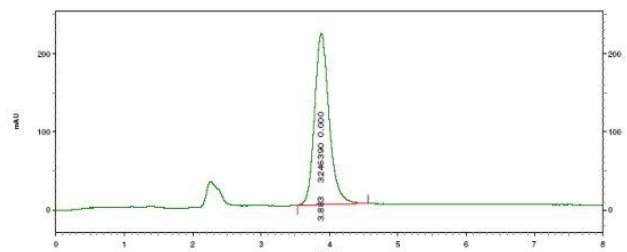
**Table 1: Details of the denture base materials used in the study**

S.No	Trade name	Details
1	Trevalon	Dentsply India Pvt. ltd, Gurgaon)
2	Trevalon Hi	
3	Acralyn-H	Asian Acrylates, Mumbai
4	DPI	Dental Products India, Mumbai

**Sample Preparation**

A total of 48 square wax blocks of 10x10x5mm were prepared using modeling wax (Hindustan dental products, Hyderabad, India) in accordance with the ISO specification 1567 (Fig 1).

**Figure 1: Flow chart showing the detailed study design and methodology.**



Prepared wax patterns were processed using conventional compression molding technique for each selected denture base material according to the manufacturer’s instructions.

Final closure was done after removal of excess flash and flask was firmly tightened under uniform pressure on a bench press with 2000psi pressure for 30 minutes. Following which, the samples for each selected denture

base material was divided into two groups and were subjected to short curing cycle (designated as Group S) and long curing cycle (designated as Group L) respectively (Table 2).

Table 2: Details of the curing cycles used in the study

Materials	Powder:Liquid Ratio	Short Curing Cycle (S)	Long Curing Cycle (L)
Trevalon	24g-10ml	Cured in boiling water for 20minutes, cooled for 20minutes and re-heated and boiled for 10minutes.	Immerse the clamped flasks in water at room temperature, apply heat gradually upto 74 <sup>0</sup> C and maintain the temperature for 7 hrs
Trevalon Hi	25g-11ml	Immerse the clamped flask in boiling water, turn off the heat and add 200ml of cold water for every 2 litres of water that was used for boiling and leave it for 60 minutes. Then re-heat gradually for 10 mins and boil for 20 minutes.	
Acralyn	30g-10ml	Immerse the clamped flasks in cold water, bring gradually to boil in 30 mins and boil for 30 mins.	
DPI	30g-10ml	Immerse the clamped flasks in water at room temperature, apply heat gradually upto 74 <sup>0</sup> C and maintain the temperature for 1½ hrs. Then immerse in boiling water for	

For both curing cycles, on completion of polymerization cycle, bench cooling was done for 30 min and the cured samples were retrieved, cleaned, and finished with 1200-grit abrasive waterproof sand paper at low speed (Sankyo Rikagaku Co Ltd, Saitama, Japan). Rigorous polishing was intentionally avoided as it would lead to evaporation of residual monomer from the acrylic specimens. After finishing and polishing procedure, the samples were separated for estimation of residual monomer at pre-determined time intervals (immediate, one day and one week) after storing them in deionized water.

**HPLC Method Development:**

A specific and sensitive HPLC Analytical method was developed and validated to estimate the residual monomer

content in the selected denture base materials after curing [12][13]. The method development was performed according to ICH guidelines Q2 (R1).

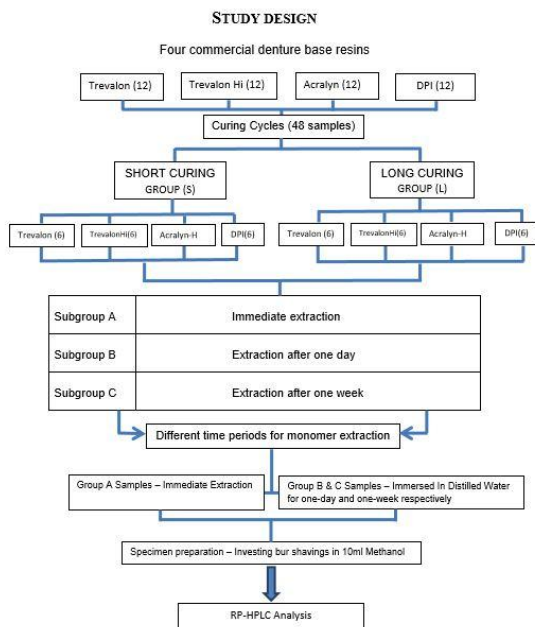
**Preparation of solutions:**

20 µl of Methyl methacrylate monomer was diluted to 5000-fold with methanol to get working stock solution. From this working stock solution, different concentrations were prepared by pipetting out 250, 325, 500, 625 and 750 µl and making the volume up to 1000µl.

The chromatographic conditions for the quantification of MMA were optimized using grace vydac C18 column (250 x 4.6 mm, 5 micron) and chromatographic separation was performed in an isocratic elution mode by feeding a mobile phase of 60% methanol with 40% MilliQ water at a flow rate of 0.8ml/min at a temperature of 23°C. Ultraviolet absorption of the column eluates was detected at a

wavelength of 205 nm. Methyl Methacrylate was quantified on the basis of a calibration graph prepared by plotting the peak height ratios to the internal standard solutions treated similarly (Fig 2).

**Figure 2: Standard chromatogram of MMA with no interference observed at the retention time (3.9 min) of MMA (1.86 µg/ml).**



**Preparation of acrylic samples for monomer estimation:**

The cured samples were ground using carbide bur at slow speed of 200rpm and the acrylic shavings were collected in a glass beaker. Acrylic shavings weighing 200mg were transferred into small vials containing 10ml of HPLC grade methanol which was chosen as the extraction solvent and were vortexed overnight for the extraction of monomer into the solvent. A micro pipette with separate volumetric tip was used to transfer a 0.2 ml aliquot of monomer containing slurry from each sample to centrifuge tubes. The slurry was centrifuged at 3000 rpm for 10 mins. The solution from the upper portion of the centrifuged tube was collected into vials using calibrated micropipette.

**Procedure of estimation of residual monomer:**

20 µl of the extracted sample was diluted 5000 fold with methanol to obtain working stock solution. These diluted samples were then analysed using HPLC. The HPLC traces were recorded with a standard data capture system. The peak area of R-MMA on the HPLC trace was determined. The area under the peak is proportional to the volume of the monomer. A standard calibration curve was obtained by plotting peak areas of five known concentrations of the MMA (cMMA) in methanol. The levels of extracted residual monomer were thus calculated using linear regression equation.

The following equation was used to calculate total amount of MMA in the sample solution, mMMA (µg):

$$m_{MMA}(\mu g) = \left( c_{MMA} \left( \frac{\mu g}{ml} \right) \times \frac{10 (ml)}{0.2 (ml)} \right) \times 10 (ml)$$

This value was used to calculate the weight percentage of the residual MMA by the following equation:

$$\text{Residual MMA monomer (wt\%)} = \frac{m_{MMA}(\mu g) \times 100}{\text{Mass of sample } (\mu g)}$$

**RESULTS**

All the analysis was performed using SPSS version 27. Descriptive analysis of the mean values was performed for comparison between the study groups for S and L cycle, at three intervals (immediate, one day and one week) using One-way Analysis of Variance (ANOVA).

The residual monomer observed with short curing cycle during the study are presented in Graph 1. For the samples of Short curing cycle, the immediate extraction group displayed the highest R-MMA content [Trealon (1.99%)>Trealon Hi (1.179%)>Acralyn (1.78%)>DPI(1.61%)]. Samples on extraction of R-MMA after one day immersion in water were Acralyn(1.355)>DPI(1.22%)>Trealon Hi(1.15%)>Trealon(0.77%). The least concentration of R-MMA was seen in the samples extracted on the seventh day with DPI (0.73%)>Trealon(0.65%)>Acralyn(0.62%)>Trealon Hi(0.57%).

The residual monomer in the samples subjected to long curing cycles is presented in Graph 2. For the samples of Long curing cycle, the immediate extraction group displayed the highest R-MMA content with Trealon Hi(2.84%)>DPI(2.05%)>Trealon (1.96%)>Acralyn(1.71%). The extraction of R-MMA after one day immersion in water were Trealon Hi(2.32%)>Trealon(1.52%)>Acralyn(1.14%)> DPI(0.87%). The least concentration of R-MMA was seen in the samples extracted on the seventh day Trealon Hi(1.56%)>Trealon(0.87%)>Acralyn(0.74%)>DPI(0.61 %).

**DISCUSSION**

PMMA’s are the most commonly used materials for removable denture fabrication [1]. A completely polymerized PMMA is an inert material and does not elicit any biological reactions [14]. However, with most processing techniques it was observed that traces of R-MMA remain in the material without undergoing polymerization [10]. The presence and leaching of R-MMA from cured denture base is known to cause hypersensitivity reactions [14][15].

The amount of R-MMA in a polymerized denture is affected by various factors such as the polymer to monomer ratio, mode of curing, the curing time and temperature, and the storage time and medium. Several studies have reported that curing cycle and storage time of the materials could have a significant effect on the R-MMA of heat cure acrylic denture base materials [8] [16].

In the present study, quantification of R-MMA was done on four commonly used heat cure denture base products using a validated HPLC method which is a sensitive and accurate method [4]. Its LOD (level of detection) is very low (0.9984), making the method very specific and sensitive for its estimation in the denture base materials. The curing of these materials involves the application of heat and pressure to the monomer-polymer dough; whereby the monomer is polymerized [16] [17]. Two curing cycles were employed, short (S) and long (L) curing cycle as it was intended to determine the additional effect of the boiling temperature on the residual monomer levels in the cured dentures.

From the results it could be observed that R-MMA of Trevalon Hi (2.84 %) was significantly higher than its counterparts in the long curing cycle. The likely reason could be that Trevalon Hi had significantly lower powder to liquid ratio compared to other products. Due to the lower powder/liquid ratios the peroxide/amine ratio will be less and hence the rate of decomposition of the peroxide will be higher. Consequently, the net effect will be a decrease in the concentration of longer-lived radicals and an increase in the R-MMA. Also, previous studies have shown that P/L ratio has a greater influence on the R-MMA [18] [19].

Interestingly, it was found that the R-MMA in samples subjected to long curing cycle was more than those cured using short curing cycle. The probable cause of such finding is the difference in the curing time and temperature. In long curing cycle, the temperature used for the polymerization of the resin was below the glass transition temperature ( $T_g$ ) of the matrix phase (97–100 °C) [20]. Therefore, the monomer did not polymerize completely due to lower molecular chain motions and immobilization of monomer in the glassy polymer [21][22], whereas in short curing cycle which had a terminal boiling, the temperature was above the  $T_g$  which increased polymerization leading to subsequently reduced R-MMA. It can be attributed to the fact that at higher temperatures, the monomer molecules could diffuse more rapidly to the polymerization active sites leading to better polymerization. Hence, for heat activated resins, processing for longer time in boiling water should reduce the monomer to an acceptable level. The R-MMA levels for heat cured denture base resins are normally about 0.3% when terminal boil is used in the curing cycle [19]. However, processing temperature should not be raised to boiling point until most of the polymerization is completed, as it may result in porous dentures. Dotjan A et al [22] and Harrison and Huggett [23] reported that a terminal boiling stage assured an optimum result in terms of R-MMA levels. The results of the present study corroborate these reports and support the findings of the study by Dotjan A *et al* [22], which showed that within the same type or brand of acrylic resin, the R-MMA decreased with curing time and temperature.

The study also intended to compare the influence of water immersion on the R-MMA for various products. From the results, it was observed that the R-MMA was found to progressively decrease with time after immersion in water. The samples after immersion in water for one day displayed lesser concentration of R-MMA compared to the immediate

extraction samples. The probable reason for such reduction could be that the water enters the polymeric chain network which leads to expansion of the material and facilitates the release of R-MMA [5][24][25]. However the reduction was highest on the first day compared to the levels achieved after one week. This can be attributed to the studies that observed most of the R-MMA to leach out from the acrylate within the first few days, but small amounts can be found in a denture even after 17 years [26][27]. However, leaching out of monomer can only be partially accounted for, as only a small quantity is lost by this method. The greater quantity of the R-MMA is hypothesized to have polymerized within the polymer [28][29]. Studies suggest that immersion in water is associated with the exclusion of oxygen, which inhibited continuing polymerization, rather than being associated with water leaching [30][31].

The results of the present study suggests that dentures produced by long curing cycle without terminal boiling contain more amount of R-MMA than those dentures processed with short curing cycle with terminal boiling indicating that the level of R-MMA in acrylic resin is influenced by the polymer-monomer ratio, the processing method and the immersion time.

#### Clinical relevance

A terminal boiling process at the end of the curing cycle will reduce the residual monomer in the cured dentures. Such a process improves the degree of polymerization in the cured denture with resultant improvement in the properties, albeit not significantly and also reduces the chances of tissue irritation due to residual monomer release.

#### Limitations of the study

The sample size of the study is small; evaluation of the residual monomer content in a larger sample size might yield more significant results.

The quantitative estimation measured was under controlled conditions which may not represent the oral cavity environment. The effect of temperature and pH of the oral fluids on the monomer release has not been evaluated in the present study.

#### CONCLUSION

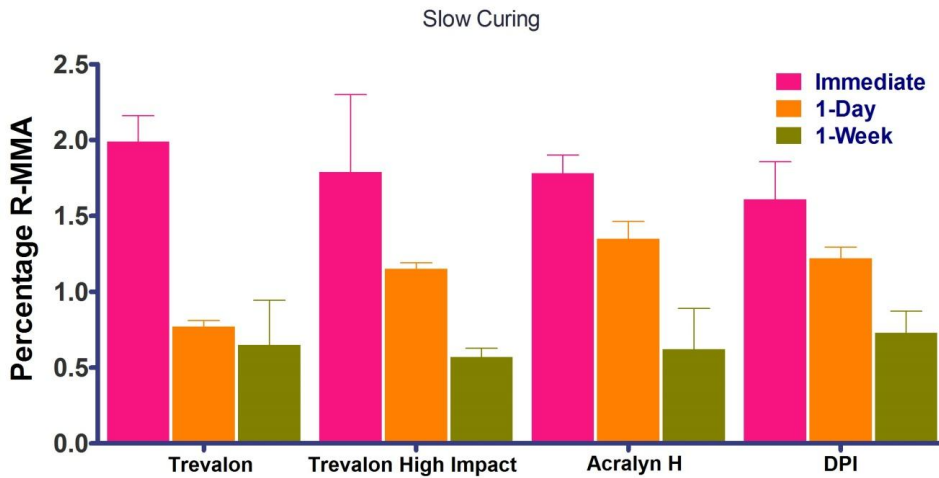
Trevalon and Trevalon Hi processed by Short curing cycle have shown increased amount of R-MMA compared to DPI and Acralyn. In samples processed through long curing cycle Trevalon Hi had the highest levels of R-MMA compared to Trevalon, DPI and Acralyn which showed similar quantity of R-MMA. However, all samples processed through short curing cycle were observed to contain lesser quantity of R-MMA compared to the samples processed through long curing cycle. This fact is attributed to the terminal boiling included in the short curing cycle. Also, all the samples have shown to have reduced quantity of R-MMA after immersion in water. This reduction of R-MMA is most for the Trevalon and Trevalon HI samples compared to DPI and Acralyn.

Within the limitations of the present study, it can be concluded that a terminal boiling process at the end of the curing cycle whether long or short cycle, can be useful in reducing the residual monomer content level in the final

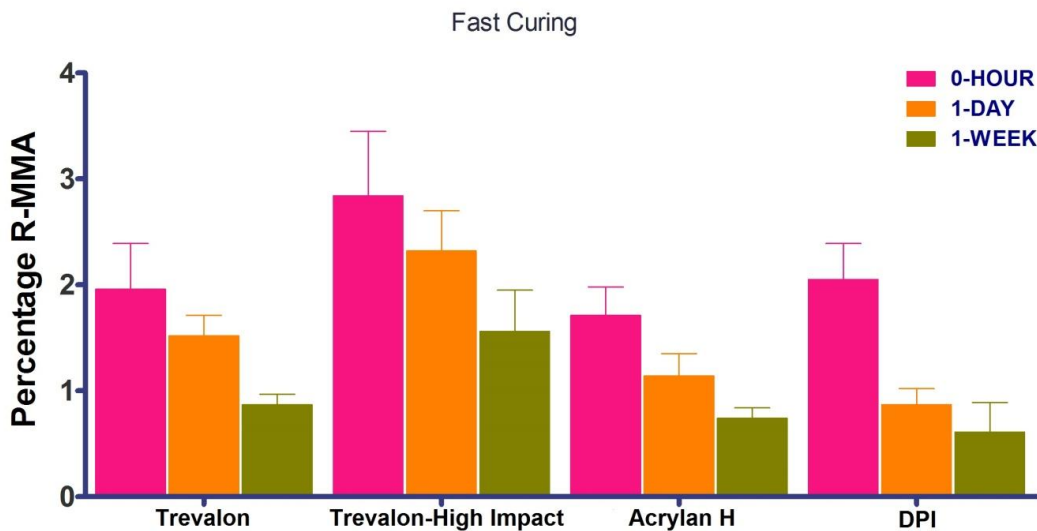
processed dentures. Immersion of the cured acrylic denture base materials in water for a day before the final denture delivery can considerably reduce the residual monomer

content and thereby avoid the potential complications due to the R-MMA.

**Graph1: R-MMA content in denture bases cured by short curing cycle**



**Graph 2: R-MMA content in denture bases cured by Long curing cycle**



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