

# Modification of curing technique of a 'self cure' injection molding acrylic resin: Effect on residual monomer

Thitiwadee Rukkhaphan<sup>1</sup>, Widchaya Kanchanasavita<sup>2</sup>, Amornrat Wonglamsam<sup>3</sup>

<sup>1</sup> D.D.S, Department of Prosthodontics, Faculty of Dentistry, Mahidol University

<sup>2</sup> D.D.S., Grad. Diploma in Clinical Science (Prosthodontics), M.Sc. (Dental Materials Science), Ph.D. (Biomaterials), Diplomate Thai Board of Prosthodontics, Department of Prosthodontics, Faculty of Dentistry, Mahidol University

<sup>3</sup> D.D.S., M.Sc., (Prosthodontics), Ph.D. (Dental Materials Science), Diplomate Thai Board of Prosthodontics, Department of Prosthodontics, Faculty of Dentistry, Mahidol University

**Objectives:** To compare residual monomer levels of a heat-cure and a self-cure injection-molding denture base materials after immersing in distilled water for 7 days. The curing process of the self-cure material was modified from that recommended by the manufacturer

**Materials and methods:** Two denture base polymers, heat-cure SR Ivocap<sup>®</sup> High Impact (Ivocap wet curing) and self-cure IvoBase Hybrid (IvoBase dry curing), were selected for this study. Three disc shaped specimens of each brand (50 mm. diameter 3 mm. thickness) were prepared from separate mixes. The mixing ratios and processing methods were achieved according to the manufacturer's instruction. Modification of the curing process of IvoBase<sup>®</sup> Hybrid was achieved by wet curing at 100 °C (IvoBase wet curing). Each specimen was immersed in 37°C distilled water at 7 days. Residual monomer was extracted from the immersed specimen and determined by gas chromatography following ISO 20795-1:2013. The freshly prepared specimens were also determined for residual monomer. Non-parametric independent sample test (Kruskal-Wallis test and Mann-Whitney U test) was used to analyze the data at  $\alpha=0.05$ .

**Results:** SR Ivocap<sup>®</sup> High Impact showed significantly higher residual monomer level than IvoBase<sup>®</sup> Hybrid after 7 days water immersion. No different residual monomer level was found when IvoBase<sup>®</sup> Hybrid was polymerized wet or dry. The residual monomer level of the specimens decreased when they were immersed in water 7 days compared to when they were not.

**Conclusions:** Different curing technique (wet and dry curing) for IvoBase<sup>®</sup> Hybrid could not reduce the residual monomer level. Water immersion in SR Ivocap<sup>®</sup> High Impact (wet curing) and IvoBase<sup>®</sup> Hybrid (wet curing) significantly decrease residual monomer level. Water immersion in IvoBase<sup>®</sup> Hybrid (dry curing) was no different residual monomer level.

**Keywords:** modification of curing process, residual monomer, injection molding denture base material, heat-cure and self-cure, water immersion

**How to cite:** Rukkhaphan T, Kanchanasavita W, Wonglamsam A. Modification of curing technique of a 'self cure' injection molding acrylic resin: Effect on residual monomer. M Dent J 2018; 38: 305-312.

## Introduction

Poly(methyl methacrylate) (PMMA)-based acrylic resin is commonly used as denture base materials. PMMA is polymerized from methyl methacrylate (MMA) monomer by an addition

polymerization reaction. During the polymerization reaction, not all of the monomers are converted into polymers. Unreacted monomers, called residual monomers, are therefore left. [1] When the denture base contacts saliva and mucosa, residual monomer leaches out from the acrylic material into the oral environment. [2] The residual

monomer can cause local and systemic reactions such as erythema, necrosis, pain and burning sensation. Allergy from the residual monomer varies among each patient. It has been reported that the residual monomer in dental acrylic resin affects its physical and mechanical properties, such as water sorption, hardness, flexural strength, dimensional stability, tensile strength, and biocompatibility. [3, 4] Therefore, it is desirable to reduce the residual MMA content in denture base materials to as low level as possible, prior to insertion in the patients. [5] The manufacturers recommend that the residual monomer content of acrylic resins be reduced by an immersion in water for 72 hours before usage. It has been found that longer water immersion reduced residual monomer released from acrylic orthodontic appliances. [6]

Toxic or allergic reactions have been related to excessive residual monomer that results from improper processing. Jorge et al. said that the amount of residual monomer decreased as the curing temperature increased. Rising temperature resulted in mobility of the molecular chains and facilitated the conversion of monomer into polymer. [7] Lung and Darvell said that the level of residual monomer can be minimized by extending curing time and applying higher temperature. [8]

According to ISO 20795-1:2013, auto-polymerizable materials have curing temperature less than 65 °C. Ivobase® Hybrid has an initial polymerization temperature of 40°C and therefore must be categorized as an auto-polymerizable material. Heat less than 100°C may cause higher

methyl methacrylate contents in polymers than heating cycles with temperatures more than 100°C. Modification of the Ivobase curing process was thus carried out in this study by using the same curing method as for Ivocap Hybrid which was cured at 100°C. In this study, the residual monomer levels of the heat-cure Ivocap, the self-cure Ivobase, and the heat-cure Ivobase injection-molding denture base materials were determined after immersing in distilled water for 7 days.

## Materials and methods

Three experiment groups of denture base polymer were determined in this study. Name of materials, Processing technique, Powder to liquid ratio are listed in Table 1

### Preparation of test specimen disc

Stainless steel molds were mounted with dental stone into the denture flasks of injection molding technique following the manufacturer instruction manuals. For each group, three specimens (diameter 50 mm. thickness 3 mm.) were prepared from separate mixes. Powder to liquid ratio and processing technique followed the manufacturer instruction shown in Table 1. Each specimen was prepared and kept in the dark in a laboratory environment for 24±5 h prior to grinding. Wet grinding was done using metallographic grinding papers equally from both side of the specimen disc until a thickness of 2.0±0.1 mm was obtained. The periphery of

**Table 1** Materials used in this investigation (n=3)

Materials	Processing	Measurement Powder : liquid
SR Ivocap® High Impact (Group 1-Ivocap wet curing)	Place mold in water, heat up to 100°C and boil it for 35 minutes. Then cool in cold water for 30 minutes.	20g : 30ml
Ivobase® Hybrid (Group 2-Ivobase dry curing)	Dry curing following the program in the automated injection unit: initial cure at 40°C then at 120°C for 35 minutes. Then cool in cold water for 15 minutes.	34g : 20ml
Ivobase® Hybrid (Group 3-Ivobase wet curing)	Place mold in water, heat up to 100°C and boil it for 35 minutes. Then cool in cold water for 30 minutes.	34g : 20ml

the specimens was ground against the 15  $\mu\text{m}$  grain metallographic grinding paper until the entire periphery was abraded and smooth. After that, the ground specimen was stored in the dark in a laboratory environment for  $24 \pm 1$  h prior to monomer extraction.

### Extraction of monomer

Each disc specimen was broken to small pieces by cutting with the nipper into the 10 ml volumetric glass flasks, its mass weighing with analytical balance to be approximately 650 mg. Acetone diluting solution was added until the total volume is 10 ml. The flask was shaken by shaking machine for  $72 \pm 2$  h at room temperature. A 2 ml aliquot of each previously prepared sample solution was pipetted to transfer to each separate 10 ml volumetric glass flask. Then 100  $\mu\text{l}$  of the I.S. solution was added. The methanol diluting solution was added to solutions to a total volume of 10 ml. Five ml of the polymer and monomer containing slurry was transferred from each of the 10 ml volumetric glass flask to centrifuge at  $3000 g_n \text{ m/s}^2$  for 15 minutes. Then 3 ml aliquot of centrifuged solution was pipetted to injection to the gas chromatography machine.

### Preparation of standard solution

Five standard solutions with concentration 120, 300, 600, 800 and 1000 ppm of MMA monomer were prepared with 100 l of the I.S. solution, and injected into gas chromatography machine.

### Gas Chromatography

A gas chromatograph (Agilent Technologies, Inc., Delaware, USA) equipped with a flame ionization detector (FID) system was used. The ZB5 column was used. The injection part for samples was in the split mode (1:50) with the temperature maintained at  $200^\circ\text{C}$  for 2 minute and reduce to  $100^\circ\text{C}$  for 5 min. (rate  $20^\circ\text{C}/\text{minute}$ ) The carrier gas (Helium) had flow rate 1.4 ml./min. The detector was carried out by a flame ionization detector with the temperature of  $250^\circ\text{C}$  and the ratio of  $\text{H}_2/\text{air}$  flow at 45/450 ml/min.

### Gas chromatogram of standard solution

The peaks of gas chromatogram were evaluated, and retention time of MMA and I.S. was determined. A scatter plot was made by plotting the concentrations of the standard solutions and the ratios of the peak area of  $A'_{\text{MMA}}$  to  $A'_{\text{I.S.}}$  of five standard solutions (Figure 1)

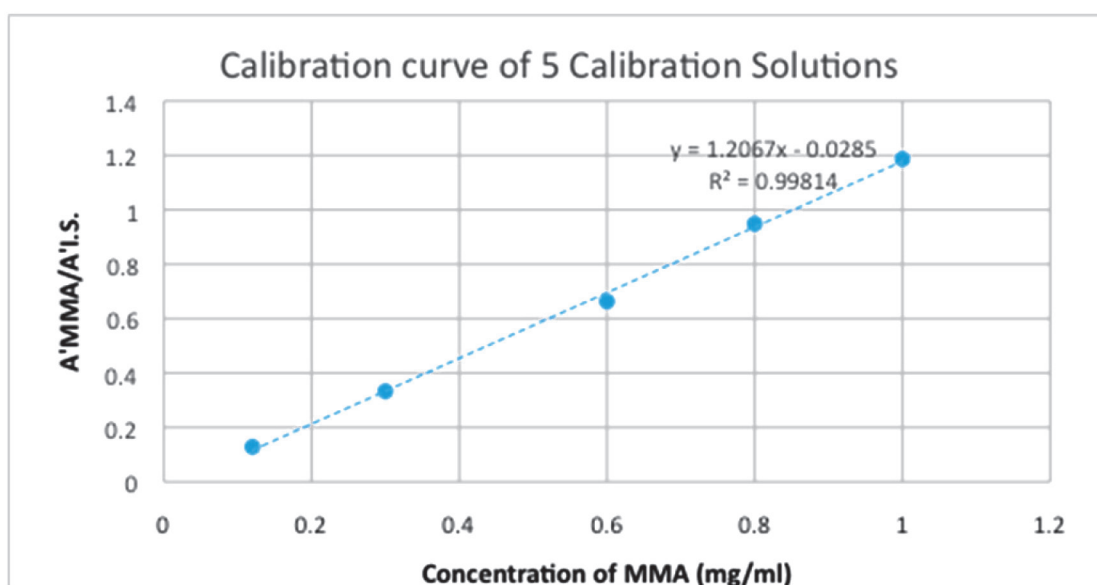


Figure 1 Concentration of MMA vs  $A'_{\text{MMA}}/A'_{\text{I.S.}}$  ratios of five standard solutions

From a scatter plot, a regression line between  $A'_{MMA}/A'_{I.S.}$  and concentration of MMA was drawn.

The equation of this regression line is  $y = 1.2067x - 0.0285$  .....Equation (1)

**Determination of residual monomer in sample solutions**

The sample solutions were injected into the column of gas chromatography machine. The peak areas of MMA and I.S. of each sample solution were recorded and the ratios of the peak areas of MMA and I.S. was calculated. The concentration of MMA ( $\mu\text{l/ml}$ ) or  $C_{MMA}$  in the sample solution was calculated using equation of regression line (Equation 1)

$C_{MMA}$  was used to calculate the amount of MMA in the sample solution ( $M_{MMA}$ ) in micrograms ( $\mu\text{g}$ ) using equation (2)

$M_{MMA} = [C_{MMA} \times (10/2) \times 10 ]$  .....Equation (2)

Then,  $M_{MMA}$  was used to compute the percentage of residual monomer by Equation (3)

Residual monomer (%) =  $M_{MMA}/M_{\text{sample}} \times 100$  .....Equation (3)

Mean residual monomer value for each specimen disc was calculated from the three sample solutions. Determination of the percentage

residual monomer was performed as a dependent variable, while the three experiment groups and the immersion/non-immersion time acted as independent variables. Non-parametric independent sample test (Kruskal-Wallis test and Mann-Whiney U test) was used to analyze the data at  $\alpha=0.05$ . The statistical analysis was done by SPSS for windows version 20.0 (IBM Corp. Released 2011. IBM SPSS Statistics for Windows, Version 20.0. Armonk, NY: IBM Corp.).

**Results**

The mean and standard deviation (S.D.) of residual monomer levels are presented in Table 2.

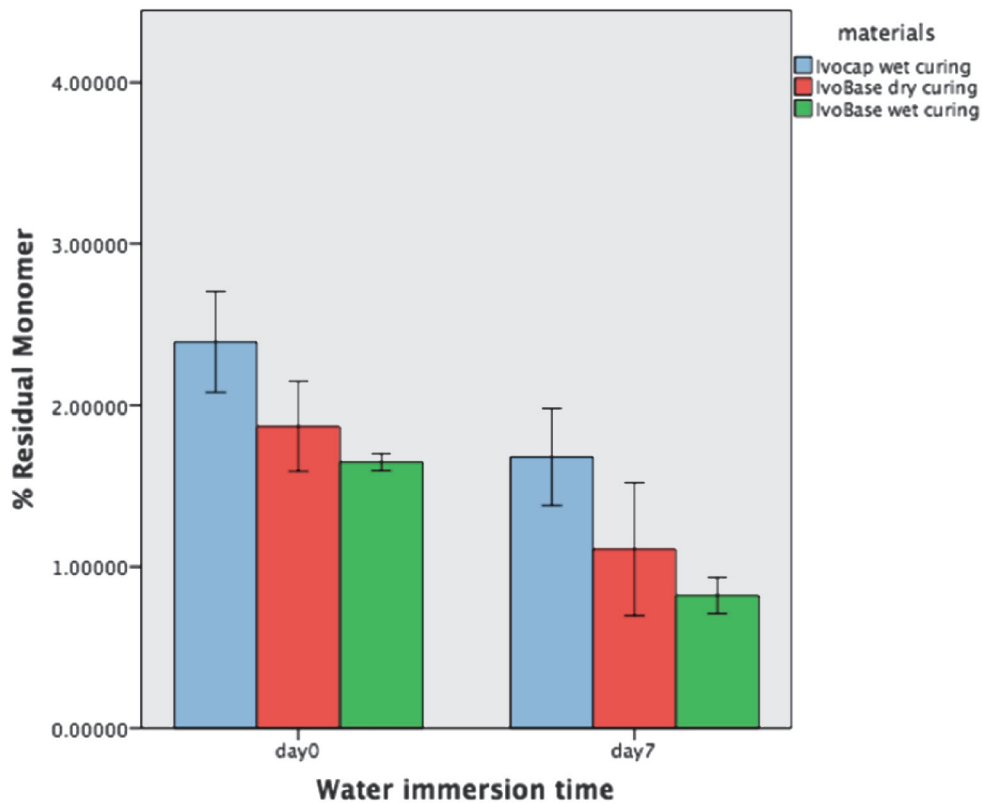
SR Ivocap® High Impact showed significantly higher residual monomer level than IvoBase® Hybrid both before and after 7 day immersion in distilled water. When IvoBase® Hybrid polymerization process was modified from that recommended by the manufacturer, the residual monomer level decreased but not significantly. Immersion in distilled water for 7 days could decrease residual monomer level significantly.

**Table 2** Percentage by mass of residual monomer level of MMA ( $\pm$  S.D.) (n=3)

Materials	Time	0 day	7 days
SR Ivocap® High Impact (Group 1-Ivocap wet curing)		2.39 $\pm$ 0.13 (A,a)	1.67 $\pm$ 0.13 (B,a)
IvoBase® Hybrid (Group 2-IvoBase dry curing)		1.86 $\pm$ 0.12 (A,ab)	1.10 $\pm$ 0.17 (A,ab)
IvoBase® Hybrid (Group 3-IvoBase wet curing)		1.64 $\pm$ 0.02 (A,b)	0.82 $\pm$ 0.04 (B,b)

\*Within the same experiment group (horizontal), the same capital superscript letter indicates no significant difference. Within the 7 day immersion and non-immersion groups (vertical), the same lower-case letters indicate no significant difference ( $\alpha = 0.05$ ), S.D. : standard deviation.

\*\* SR Ivocap® High Impact; polymerization in boiled water at 100°C (Ivocap wet curing) and two groups of IvoBase® Hybrid; polymerization via injection machine at 120°C (IvoBase dry curing) and polymerization in boiled water at 100°C (IvoBase wet curing)



**Figure 2** Percentage residual monomer levels among three experiment groups and water immersion time.  
 \* SR Ivocap® High Impact; polymerization in boiled water at 100°C (Ivocap wet curing) and two groups of Ivobase® Hybrid; polymerization via injection machine at 120°C (Ivobase dry curing) and polymerization in boiled water at 100°C (Ivobase wet curing)

## Discussion

There are many commercial injection-molding denture base materials available in dental market, which are claimed to have improved physical and mechanical properties. They were claimed to have simple processing technique, reduced producing time and reduced residual monomer levels that cause local and systemic reactions to oral cavity [2] and have an effect on mechanical properties. Undurwade and Sidhaye [9] reported that pressure have an effect in accelerating initial polymerization that results in minimal residual monomer level content and preventing porous formation in the materials. [10] From the manipulation aspect, dentures made from injection molding

technique is more difficult to fabricate and has higher costs than the compression molding technique. It requires highly trained technician, complex mould design, and uses complicated and expensive equipment. Then, inadequate spruing might result to incomplete molds. However, it has instant prepacked-cartridge form and easy to rapid mechanical mixing and curing equipment that result in homogeneous mixture.

SR Ivocap High Impact® chosen for this study was a heat-cured injection molding denture base material because it requires curing temperature at 100°C in water (Type 1: Heat-polymerizable materials classified by ISO 20795). [11] Ivobase Hybrid was claimed by the manufacturer to be a self-cured injection molding denture base materials because of the curing temperature

at 40°C. However after the initial cure at 40°C the temperature was increased up to 120°C for 35 minutes. Therefore, Ivobase material is actually the heat-cure material. In this study the curing of Ivobase was modified to resemble that of Ivocap High Impact (- heat up to 100°C and boil it for 35 minutes).

The residual monomer level of denture base polymers from the previous study [12] varied due to the difference in the polymerization procedures and the experimental condition. Some MMA was lost during polymerization and monomer extraction process because it was an experiment under open system. [8] In this study, the specimen preparation, monomer extraction and determination of residual monomer content followed the ISO 20795-1:2013 Part 1: Denture base polymers. [11]

During fabrication, the specimen was ground and polished from 3 mm. to 2 mm. thickness (ISO 20795-1:2013). [11] Polishing may decrease the residual monomer level compared to the non-polished specimens because of the frictional heat which may increase the temperature of the specimen, causing monomer loss. [13] In this study, the specimen discs were carefully ground and polished using adequate lubricant to avoid frictional heat during polishing. In this study, a nipper was used to break the specimen discs into small pieces instead of drilling or cutting by a bur that can cause frictional heat. [11] Polymerization of Ivobase Hybrid at 100°C boiling water instead of at 40°C in the Ivocap machine was expected to reduce the material monomer content. Actually the residual monomer level did decrease but not significantly.

There are several methods for determining the residual monomer level such as bromine titration, Fourier transform infrared (FT-IR), high performance liquid chromatography (HPLC) and gas chromatography (GC). [14] This investigation chose gas chromatography because of the high volatility of the monomer, simplicity, rapidly and high reproducibility. [15]

Monomer extraction was made under open system. [8] The ISO 20795-1:2013 [11] suggested using the stirring machine in monomer extraction. However, there was a limitation in instruments so we decided to use the shaking machine without stirring rods instead of stirring machine in this study.

Residual monomer determination procedure in this study was modified from the procedure in the ISO 20795-1:2013 [11] by using the ZB5 column because we could not create the peak area of MMA. The injection part for samples was in the split mode (1:50) with the temperature maintained at 200 °C for 2 minute and then reduced to 100 °C for 5 min. (rate 20 celcius/minute). The carrier gas (Helium) had flow rate 1.4 ml./min. The detector was carried out by a flame ionization detector with the temperature of 250 °C and the ratio of H<sub>2</sub>/air flow at 45/450 ml/min. These operating conditions could measure the amount of the residual monomer. [2]

Previous studies reported that increasing curing temperature had an effect on residual monomer level. Jorge et al. [7] said that the amount of residual monomer decreased as the curing temperature increased, rising temperature resulting in mobility of the molecular chains and facilitating the conversion of monomer into polymer. Lung and Darvell [8] said that the level of residual monomer can be minimized by extending curing time and applying higher temperature. However, this investigation found that there was no significant difference of the residual monomer level when Ivobase Hybrid was polymerized differently (Group 2 and 3).

SR Ivocap High Impact has residual monomer level greater than Ivobase Hybrid wet curing. This might be because SR Ivocap High Impact (powder to liquid ratio 20g : 30 ml) [16] has lower amount of powder to liquid ratio than Ivobase Hybrid (powder to liquid ratio 34g : 20 ml). [17] The higher proportion of polymer to monomer reduced residual monomer level. [18]

The manufacturers instructions recommend that the residual monomer content acrylic resins be reduced by an immersion the polymerized materials in water for 72 hours before usage. [6] Baker et al [19] suggested to immerse the removable appliance in water for at least 25 hours before insertion to reduce the risk of irritant from residual monomer. This study compared immersion time at no water immersion and 7 days of water immersion. The results showed that the residual monomer level of SR Ivocap High Impact and IvoBase Hybrid wet curing were significantly decreased when immersed in water for 7 days. This might be because the residual monomer leaches out of the denture base materials into surrounding liquid medium, be it water or saliva. IvoBase Hybrid used in this study passed the biosafety criterion according to ISO 20795-1:2013 [11] specification that suggested that a standard acceptable maximum level of residual monomer of denture base type 1 not to exceed 2.2% by mass fraction.

Within the limitations of this study, it can be concluded that:

Different curing technique (wet and dry curing) for IvoBase Hybrid could not reduce the residual monomer level. Water immersion in SR Ivocap High Impact (wet curing) and IvoBase Hybrid (wet curing) significantly decrease residual monomer level. Water immersion in IvoBase Hybrid (dry curing) was no different residual monomer level.

## References

1. K A, C S, H R. Phillip's Science of Dental Materials. 12 ed. Missouri: Elsevier Inc; 2013.
2. Kedjarune U, Charoenworluk N, Koontongkaew S. Release of methyl methacrylate from heat-cured and autopolymerized resins: cytotoxicity testing related to residual monomer. *Aust Dent J* 1999; 44: 25-30.
3. Jerolimov V, Brooks SC, Huggett R, Stafford GD. Some effects of varying denture base resin polymer/monomer ratios. *Int J Prosthodont* 1989; 2: 56-60.
4. Stafford GD, Brooks SC. The loss of residual monomer from acrylic orthodontic resins. *Dent Mater* 1985; 1: 135-8.
5. Bayraktar G, Guvener B, Bural C, Uresin Y. Influence of polymerization method, curing process, and length of time of storage in water on the residual methyl methacrylate content in dental acrylic resins. *J Biomed Mater Res B Appl Biomater* 2006; 76: 340-5.
6. Nik TH, Shahroudi AS, Eraghizadeh Z, Aghajani F. Comparison of residual monomer loss from cold-cure orthodontic acrylic resins processed by different polymerization techniques. *J Orthod* 2014; 41: 30-7.
7. Jorge JH, Giampaolo ET, Machado AL, Vergani CE. Cytotoxicity of denture base acrylic resins: a literature review. *J Prosthet Dent*. 2003;90(2):190-3.
8. Lung CY, Darvell BW. Minimization of the inevitable residual monomer in denture base acrylic. *Dent Mater* 2005; 21: 1119-28.
9. Undurwade JH, Sidhaye AB. Curing acrylic resin in a domestic pressure cooker: a study of residual monomer content. *Quintessence Int* 1989; 20: 123-9.
10. Yau WF, Cheng YY, Clark RK, Chow TW. Pressure and temperature changes in heat-cured acrylic resin during processing. *Dent Mater* 2002; 18: 622-9.
11. International Organization for Standardization. ISO 20795-1:2013[E], Dentistry – Base polymers – Part 1. ISO Geneva, Switzerland. 2013.
12. Bartoloni JA, Murchison DF, Wofford DT, Sarkar NK. Degree of conversion in denture base materials for varied polymerization techniques. *J Oral Rehabil* 2000; 27: 488-93.
13. Vallittu PK. The effect of surface treatment of denture acrylic resin on the residual monomer content and its release into water. *Acta Odontol Scand* 1996; 54: 188-92.
14. McCabe JF, Basker RM. Tissue sensitivity to acrylic resin. A method of measuring the residual monomer content and its clinical application. *Br Dent J* 1976; 140: 347-50.
15. Lung CY, Darvell BW. Methyl methacrylate in poly(methyl methacrylate)--validation of direct injection gas chromatography. *J Chromatogr A* 2004; 1061: 93-8.
16. Safety Data Sheet acc. to OSHA HCS. SR Ivocap High Impact Polymer. Ivoclar Vivadent Inc.; 2015.

17. Safety Data Sheet acc. to OSHA HCS. IvoBase Hybrid Monomer. Ivoclar Vivadent Inc.; 2015.
18. Vallittu PK, Ruyter IE, Buykuilmaz S. Effect of polymerization temperature and time on the residual monomer content of denture base polymers. *Eur J Oral Sci* 1998; 106: 588-93.
19. Baker S, Brooks SC, Walker DM. The release of residual monomeric methyl methacrylate from acrylic appliances in the human mouth: an assay for monomer in saliva. *J Dent Res* 1988; 67: 1295-9.