THE LEVEL OF RESIDUAL MONOMER IN INJECTION MOLDED DENTURE BASE MATERIALS

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Statement of Problem : The residual monomer of denture base materials causes hypersensitivity on oral mucosa and intereferes with the mechanical properties of the cured resin. The amount of residual monomer is influenced by materials, curing cycle, processing method, and etc.

Purpose : The aim of this study was to investigate the residual methyl methacrylate(MMA) content of injection molded denture base polymer, and to compare this with the self-cured resin and the conventional compression molded heat-cured resin.

Materials and Methods : Disc shaped test specimens (50mm in diameter and 3mm thick) were prepared in a conventional flasking technique with gypsum molding. One autopolymerized denture base resins (Vertex SC. Dentimex. Netherlands) and two heat-cured denture base resins (Vertex RS. Dentimex. Netherlands, Ivocap. Ivoclar Vivadent, USA) were used. The three types of specimens were processed according to the manufacturer's instruction. After polymerization, all specimens were stored in the dark at room temperature for 7 days. There were 10 specimens in each of the test groups. 3-mm twist drills were used to obtain the resin samples and 650mg of the drilled sample were collected for each estimation. Gas chromatography (Agillent 6890 Plus Gas Chromatograph, Agillent Co, USA) was used to determine the residual MMA content of 10 test specimens of each three types of polymer.

Results : The residual monomer content of injection molded denture base resins was $1.057 \pm 0.141\%$. The residual monomer content of injection molded denture base resins was higher than that of compression molded heat cured resin ($0.867 \pm 0.169\%$). However, there was no statistical significant difference between two groups ($p > 0.01$). The level of residual monomer in self cured resin(3.675 ± 0.791) was higher than those of injection molded and compression molded heat cured resins ($p < 0.01$).

Conclusion : With respect to ISO specification pass/fail test (2.2% mass fraction) of residual monomer, injection molding technique($1.057 \pm 0.141\%$) is a clinically useful and safe technique in terms of residual monomer.

Key Words
Residual monomer, Injection molding, Denture base, Gas chromatography

Acrylic resin polymers were introduced as a denture base material in 1937. Nowadays the majority of dentures are made of heat-cured polymethyl methacrylate(PMMA). Polyme- rization of PMMA can be started by heating the polymer -monomer mixture in a water bath, and by chemical activation. The goal of conventional rapid curing of acrylic resins is to completely polymerize the resin without porosity. In the conventional rapid curing methods, the monomer molecules are moved by thermal shocks from other molecules and passively moved to polymer chain due to external heat. During polymerization the monomer is reduced. As the temperature increases, molecular mobility speeds up, leading to more complete polymerization. All acrylic resins contain variable residual monomer levels depending on the ambient conditions and the efficiency of heat transfer. Flory[1] characterizes the process as a combination of effective monomer diffusion, exothermic heat, and chain mobility to autoaccelerate the MMA conversion to PMMA. Residual monomer may diffuse from acrylic resin to saliva resulting in irritation of allergic side effects.[2,3] For acrylic resins to induce a primary irritation of sensitization, free monomer must be leached out. Proper processing techniques minimizes residual monomer in the range of 1-3% which is well tolerated by most individuals.[4] It has also been reported that a high level of residual monomer is detrimental to mechanical properties of the cured resins.[5] Many investigations have demonstrated that residual monomer content varied considerably with curing conditions, and the amount of residual monomer was one of the primary factors affecting the properties of denture base materials produced under different curing cycles. There are many factors that influence the level of residual monomer: curing cycle, processing method, thickness of denture base, immersion in water, period of usage, surface treatment.[6-10] In this study the effect of one of molding method, injection molding technique, was investigated.

Compression molded methylmethacrylate has been the standard denture base material for more than 60 years. Undesirable dimensional changes that occur during processing by this method have been thoroughly documented.[11] More recently, an injection molding technique, the SR-Ivocap System (Ivoclar USA Inc., San Marcos, Calif.) demonstrated some advantages such as minimal changes in vertical dimension and enabling the processing a large maxillary obturator[12]. A continuous pressure injection technique has been developed to reduce processing error and increases resin density through layered polymerization of the resin with no processing flash. The use of prepacked liquid/powder capsules, a mechanical mixing procedure, and injection of mixed resin into the flask under continuous pressure during processing help produce a homogenous denture. Improved dimensional stability, better control of polymerization shrinkage, and reduced vertical dimension of occlusion changes have been demonstrated with injection-processed prostheses compared with those fabricated with the conventional compression molding technique. Specifications of the continuous pressure injection technique for processing PMMA have been investigated, with hi-gloss polished surfaces and homogeneous structures being attributed to prepacked PMMA capsules and rapid mechanical mixing.

Previous reports on the injection molding system generally regarded with the dimensional accuracy and the opening of the vertical dimension of occlusion.[13-21] But there is few report on residual monomer in injection molding processing methods. One of them reported that there was no significant difference between conventional heat and pressure technique and an injection molding system at room temperature under pressure (Intopress, Kulzer Co. Germany).[22]

The aim of this study was to investigate the effect of injection molding on the residual methyl methacrylate (MMA, 2-propenoic acid, 2-methyl-, methyl ester) content of denture base polymer.

MATERIALS AND METHODS

1. Materials

Three denture base resins, specially formulated for polymerization by different methods, were compared under the processing conditions listed (Table Ⅰ). These included a rapid-polymerized resin Vertex RS, which is not a conventional long cure resin as a control group, because the experimental group Ivocap is a rapid-polymerized resin(Fig. 1).

2. Specimens, Sampling

Baseplate wax, with dimensions of 50mm in diameter and 3mm thick was invested in the denture flasks. Ten samples of each resin-polymerization method were prepared independently. The resins were processed according to the manufacturer's recommendation(Table Ⅰ). Finally disc shaped test specimens were prepared (Fig. 2.a). After polymerization, all specimens were stored in the dark at room temperature for 7 days. A 3-mm twist drill was used to obtain the samples. The drill was taken slowly through the specimen, and 650mg of the drilled sample were collected for each estimation (Fig. 2.b).

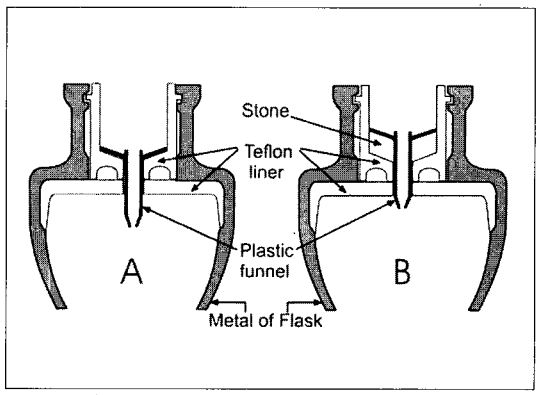


Fig. 1. Schematic drawing of injection molding of SR-Ivocap.

Table I. Denture base materials

Materials	Manufacturers		Curing modes			
			P/L ratio	mixing time	doughing time	polymerization
Vertex SC	Dentimex.	Netherlands	7 : 2	10 seconds	5 minutes	20C, 10minutes
Vertex RS	Dentimex.	Netherlands	3 : 1	10 seconds	10 minutes	100C, 20 minutes
SR-Ivocap	Ivoclar	Vivadent USA	20g/30ml	5 minutes	10 minutes	100C, 35 minutes

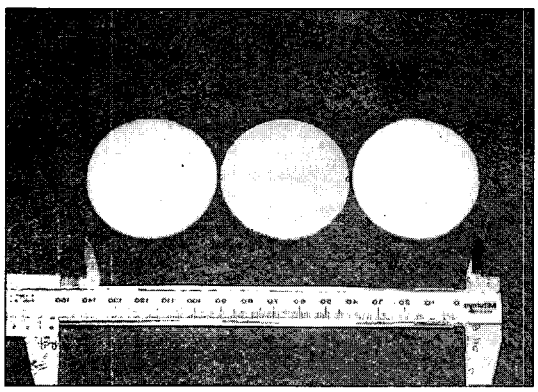


Fig. 2. a) Specimens.

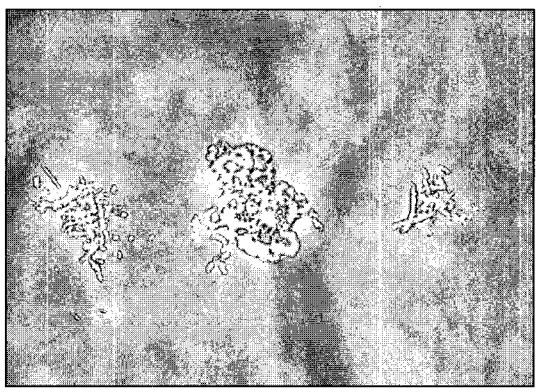
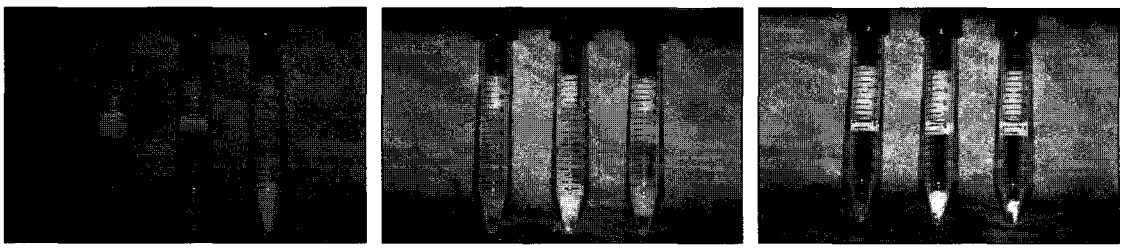


Fig. 2. b) Drill cuttings.

3. Extraction

To extract the residual MMA from the polymers, 650mg of the polymers were weighed and treated with 10ml of acetone. The sample solution was fluxed by orbital shaker (Seolin. Korea) at room temperature. A 2ml aliquot of each sample solution was transferred to a tube. Then 0.1ml of an internal standard solution of n-butanol in methanol(35mg/ml) was added. Methanol solution was added to the sam-



a) b) c)

Fig. 3. a) Sample solution, b) After precipitation, c) After centrifugation.

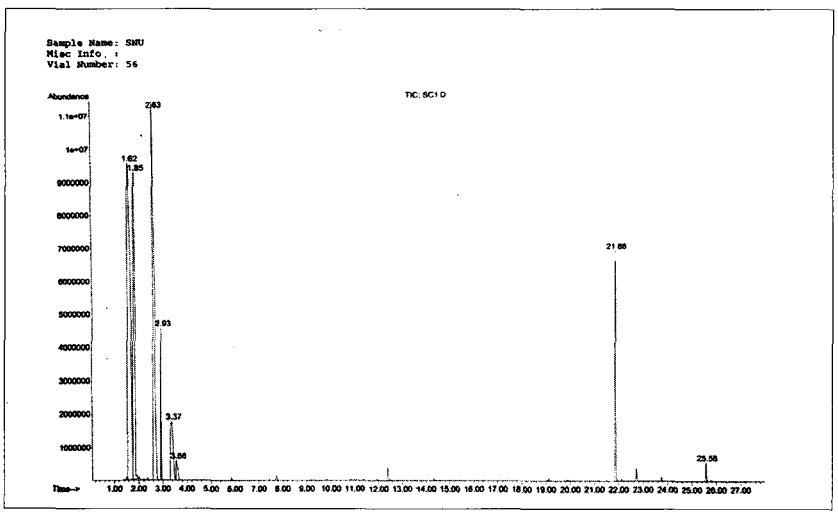


Fig. 4. A typical chromatogram, Peak of butanol(Internal standard) -retention time 2.9min. · monomethylmethacrylate - retention time 3.3min.

Table II. Peak area.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.618	108	114	124	VV	9303877	739672851	100.00%	36.384%
2	1.848	124	131	140	VV 2	9707156	426523842	57.66%	20.981%
3	2.634	184	189	203	BB	11451685	538371118	72.79%	26.482%
4	2.919	206	210	221	BB	3980887	73402901	9.92%	3.611%
5	3.366	236	243	254	BV	1344687	93261741	12.61%	4.588%
6	3.555	254	257	271	VB	588847	30316753	4.10%	1.491%
7	21.875	1605	1609	1621	BB	5907445	116773428	15.79%	5.744%
8	25.575	1875	1882	1894	BB	566852	14624452	1.98%	0.719%

ple solution to a total volume of 10ml for precipitation of dissolved polymer. 5ml of the dissolved polymer slurry were centrifuged at 5000 rpm for 10 min in a centrifuge. A 3ml aliquot of the centrifuged sample solution was transferred to a separate closed 15ml polyprophylen conical tube(Fig. 3).

4. Measurement of MMA concentration from gas chromatographic recordings

The residual MMA content was determined with a gas chromatography(GC) (Agillent 6890 Plus Gas Chromatograph, Agillent Co, USA) (Fig. 4). The chromatographic column was nonpolar (length: 30m; internal diameter: 0.25mm) and the Mass Spectrometer(Agillent 5973 MSD, Agillent co, USA) was used as the detector. Helium was used as the carrier gas. The concentration of MMA was determined using a standard calibration curve. The total quantity of MMA in the sample solution and in the test specimens was calculated with the proportion of internal standard (Table Ⅱ).

5. Determination of residual MMA by the use of internal standards.

Percentage of residual monomer calculated by following equation

: $A_{MMA}/A_{I.S.} \times 0.35mg/ml \times 10/2 \times 10/650 \times 100$ (2.69)

A_{MMA} = peak area of MMA

$A_{I.S}$ = peak area of internal standard

0.35 = correlation coefficient

10/2 = 2ml aliquot of each sample solution

10 = total volume of 10ml methanol solution.

650 = weight of sample

6. Statistical analysis

The statistical analysis was done by SPSS for window. The mean residual MMA contents were compared by one-way ANOVA in which the processing method was used as the independent variable. And residual MMA content as the dependent variable. Scheffe test was used for Post Hoc test.

RESULTS

Calibration solution was shown on Table Ⅱ. Calibration solutions were produced using standard solutions containing known amounts of monomethylmethacrylate in methanol.

Fig. 5, 6 and 7 shows the residual MMA content in the autopolymerized denture base polymers, compression molded heat-cured resin, and injection molded heat-cured resin. The mean residual MMA content in autopolymerized resins was considerably higher than those of the other two types of resins. ($p<0.01$) (Fig. 5, Table Ⅱ). The residual monomer con-

Table III. Calibration solution

MMA concentration(mg/ml)	$A_{MMA}/A_{I.S.}$	Correlation coefficient.	$A_{MMA}/A_{I.S.}$ *0.35mg/ml
0.02	0.05	0.36	0.017
0.12	0.73	0.33	0.16
0.30	0.88	0.34	0.31
0.60	1.62	0.37	0.56
0.80	2.42	0.33	0.84

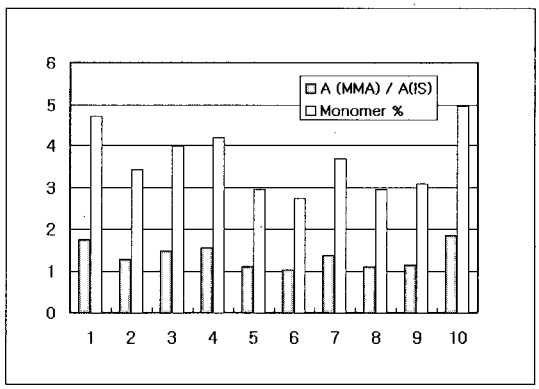


Fig. 5. Residual monomer of Vertex SC.

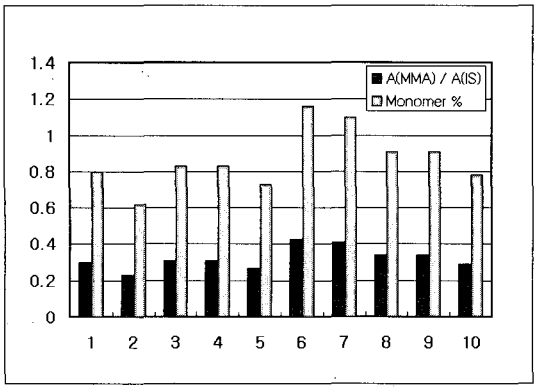


Fig. 6. Residual monomer of Vertex RS.

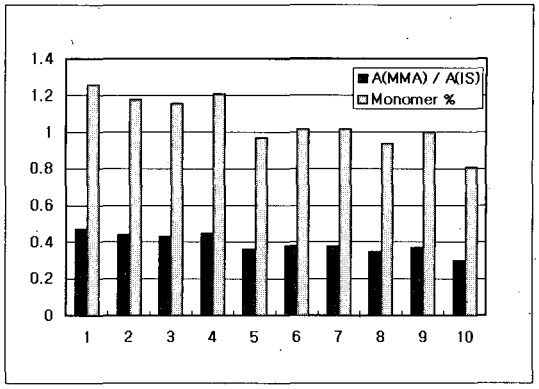


Fig. 7. Residual monomer of SR-Ivocap.

Table IV. ANOVA, Post Hoc test

ANOVA

	Sum of squares	df	Mean square	F	Sig.
Between groups	49.250	2	24.625	112.578	0.000
Within groups	5.906	27	0.219		
Total	22.155	29			

Post Hoc Tests

			Mean Difference	Std. Error.	Sig.
Scheffe	SC	RS	2.8080	0.2092	0.000
		Ivocap	2.6180	0.2092	0.000
	RS	SC	-2.8080	0.2092	0.000
		Ivocap	-0.1900	0.2092	0.666
	Ivocap	SC	-2.6180	0.2092	0.000
		RS	0.1900	0.2092	0.666

tent in injection molded denture base resins was higher than those of compression molded heat cured resin, but there was no statistically significant difference between two groups ($p>0.01$) (Fig. 6, 7, Table Ⅲ).

DISCUSSIONS

Conventionally, when denture curing process was completed, dentures were stored in water. Vallitu et al[23] investigated MMA release of chemical-cured PMMA and heat-cured PMMA in water. They showed that the amount of residual monomer decreased in water after 1 to 2 days. Therefore in this study, specimens were stored in dry dark place to prevent monomer loss. In this study, collecting the sample was done by hand drilling. Austin and Basker[24] showed that there is no significant difference in respective monomer levels when specimens were sampled at four widely different drill speeds. It seems that monomer ther-

mal degradation and evaporation during drilling were negligible. Sadamori et al[25] investigated the several solvents of MMA. They showed that the suitable solvents for extraction of the monomer from cured resin such as ethyl acetate, acetone and methyl ethyl ketone are similar in structure to MMA. Therefore acetone was used as the solvent for extraction in this study. Several physical and chemical methods have been used to measure the level of residual monomer of PMMA resin. McCabe and Basker[2], and Dogan et al[26] used gas-liquid chromatography to show that the level of the residual monomer is inversely related to the curing time. Vallitu et al[27] used high performance liquid chromatography to investigate water release of residual monomer. Austin and Basker[24] compared the residual monomer level obtained by gas chromatography(GC) and IR-spectral analysis (IR) for 12 specimens that had been cured for different curing time. The results range from 0,24 to 6.33% for GC and 0.33 to 5.50% for IR measurements. The agreement for each of the specimens was considered to be acceptable. Gas chromatography is an established method for determination of residual monomer of denture base polymers in its simplicity and rapidity.[28]

The residual monomer contents of Vertex SC, RS, & Ivocap agree with previous studies.[9,24] In these studies, the residual monomer contents are influenced by polymerization time. Generally the residual monomer contents decrease when increasing curing time. The two types of heat cured resin(both short cure technic) show higer level of monomer than that of long cure technique. Polymerization time of Ivocap (35min) is longer than Vertx RS(20min), but residual monomer level of Ivocap was slightly higher (RS-mean 0.867 ,Ivocap-mean 1.057). It may be due to different amount of cross-linking agent (Ivocap : 5.6%, RS < 5). The cross-linking agents of the denture base polymers may affect the residual monomer content of the polymer. The final conversion of MMA with a cross-linking agent decrease with increasing content of the cross-linking agent. This is due to the cross-linked main chain segments, which are bound together via the cross-linking agent. A rigid polymer structure thus hinders the conversion of MMA monomers, especially at curing temperatures lower than glass transition temperature(Tg).[29]

The residual MMA content of the heat-cured denture base polymers was considerably lower than that of the autopolymerized denture base polymers(Tg-67 to 78 C). This can be explained by the higher curing temperature, which can be as high as the glass transition temperature of the matrix phase of the heat cured denture base polymer (Tg-97 to 100 C). Above the Tg of the polymer, the monomers of the resins have a better ability to polymerize due to higher molecular chain motions and neutralization of the immobilization of MMA in the glassy polymer at higher temperatures[30].

The residual MMA content of denture base polymers is also influenced by denture thickness. The heat evolved during the polymerization reaction would cause the thicker specimen to reach higher temperatures and result in a greater degree of polymerization and also the reduction in the amount of residual monomer. In this study thickness of specimen was 3mm, and mean monomer level was 0.867%, 1.057% respectively, which corresponds with previous studies(4,5mm-mean 0.72%, 3mm-mean 1.1, 1.5mm-mean 1.4 %).[31]

CONCLUSIONS

In this study, gas chromatography was used to investigate the residual monomer in autopolymerized, compression molded, and injection molded resins. Based on this study the following conclusion could be made.

1. The residual monomer content of injection molded denture base resins was $1.057 \pm 0.141\%$.
2. The residual monomer content of injection molded denture base resins was higher than that of compression molded heat cured resin($0.867 \pm$

0.169%). but there was no statistically significant difference between two groups ($p>0.01$).

3. The level of residual monomer in self cured resin(3.675 ± 0.791) was higher than those of injection molded and compression molded heat cured resins ($p<0.01$).
4. With respect to ISO specification pass/fail test (2.2% mass fraction) of residual monomer, injection molding technique ($1.057 \pm 0.141\%$) is a clinically useful and safe technique in terms of residual monomer.

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