The Role of Residual Monomer in PMMA Powder and Methods of Polymerization in the Finding of Residual Monomer in Poly(methylmethacrylate) Denture Base

Vjekoslav Jerolimov*
Jurica Krhen**
Josip Bešić***

* Department of Removable Prosthodontics, Zagreb University School of Dentistry, Zagreb
** Milan Milanović Dental Polyclinic, Zagreb
*** Zagreb Institute of Health Care, Zagreb

Uloga ostatnog monomera PMMA-praška i metode polimerizacije u nalazu ostatnog monomera polimetilmetakrilatne protezne baze

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Summary

The amount of residual monomer in methylmethacrylate resins used for denture bases is directly dependent on the polymerization procedure chosen. Residual monomer in PMMA powder has not yet been fully clarified. The aim of this study was to determine the amount of residual monomer in some PMMA powders used for denture bases. The study included determination of the amount of residual monomer in specimens polymerized by various methods of polymerization, attepting to test the interrelationship between the finding of residual monomer in PMMA powder and the respective group of heath-cured resin specimens.

Materials from the group of poly(methylmethacrylate) resins type I, class 1 (1 – Biocryl R, Galenika, Belgrade–Zemun, and 2 – Major Base R, Major Dental Industry, Torino) were used in the study. Experimental specimens were divided into two groups: (1) original PMMA powders; and (2) polymerized specimens obtained by two short curing cycles (a – fractional, classical, heterogeneous polymerization; b – using the Prestherm, Bego device) and three long-curing cycles of polymerization (a – 14 h at 70°C; b – 7 h at 70°C and 3 h at 100°C; and c – 14 h at 70°C and 3 h at 100°C). By 2 g of each powder/specimen were extraced with methanol for residual monomer to be demonstrated by a modified method of gas chromatography on a device manufactured by Perkin Elmer Co. (Norwalk, Conn., USA).

Original PMMA powders contained a high but varying percentage of residual monomer. Polymerized specimens had significantly lower values of residual monomer as compared to PMMA powders.

Short-curing cycles were observed to leave quite high amounts of residual monomer behind, these amounts being lower when an original PMMA powder had a lower value of free monomer, which may be of some practical importance. A polymerization cycle taking

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7 h at 70°C and 3 h at 100°C resulting in negligible amounts of residual monomer is thus recommended.

Key words: *residual monomer, PMMA powder, short-cycle polymerization, long-cycle polymerization, gas chromatography.*

Introduction

Most removable dentures currently used are made by a conventional method of polymerization of biphasic resins already used for almost six decades. Besides their high qualities, numerous shortcomings, among them residual monomer, have also been described in literature.

Investigations have shown that polymerization of methylmethacrylate is never quite complete, not even with a long-curing cycle of polymerization. Some residual, non-polymerized monomer can always be found, at least in minimal amounts. Residual monomer may adversely affect both mechanical and physical properties of the denture base resin (1, 2) or elicit some toxic or allergic side-effects on oral mucosa, primarily on denture-bearing mucosa (3–5).

The degree of resin polymerization and the finding of residual monomer are directly dependent on the method of polymerization chosen, the content and ratio of PMMA powder and MMA-liquid, and some other elements (6–9).

Some previous studies have pointed to the interesting fact that a certain amount of residual monomer can be detected in acrylate resin PMMA powder (7). Therefore, the aim of this study was to assess the amount of residual monomer in some PMMA powders used for denture base construction, and to detect the possible differences. At the same time, the amount of residual monomer in specimens obtained by various heath-curing procedures was measured, and interrelationship between the findings of residual monomer in PMMA powder and in the respec-

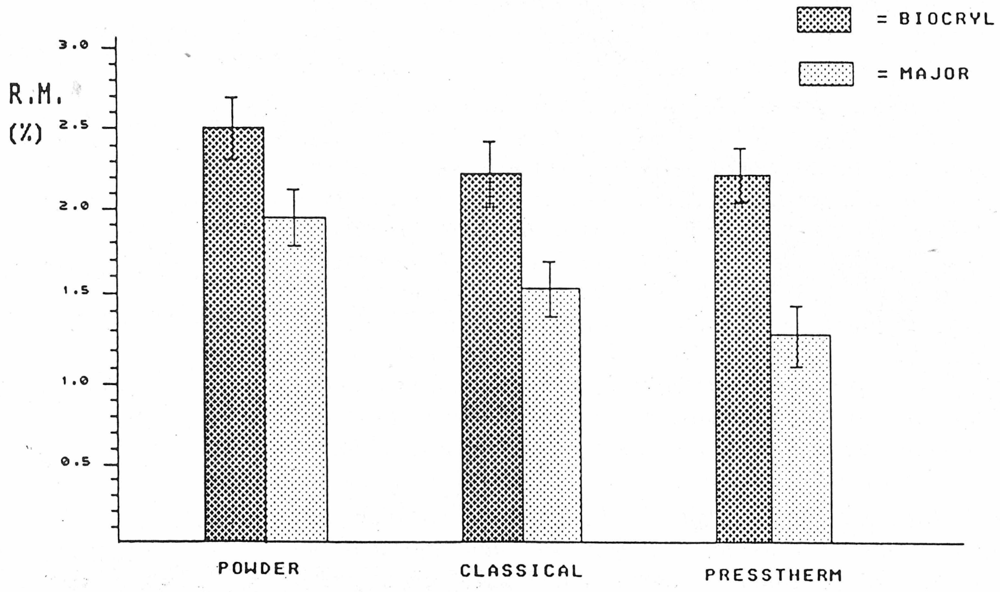

Fig. 1. *Histograms of the residual monomer levels for PMMA-powder and two short curing cycles of the materials under study*

Slika 1. *Histogramski prikaz nalaza ostatnog monomera za PMMA-prašak i dva kratkotrajna polimerizacijska postupka istraživanih materijala* tive group of heath-cured resin specimens assessed.

Material and methods

Materials from the group of poly(methylmethacrylate) resins type I, class 1 (FDI specification No. 3, ADA Standard No. 12): (1) Biocryl R (Galenika, Belgrade), and (2) Major Base R (Major Dental Industry, Torino), were used in the study.

Experimental specimens were divided into two groups: group 1 consisted of six original PMMA powder specimens, 2 g each, separately for each material under study; and group 2 consisted of specimens, dimensions 80 x 50 x 3 mm, obtained from acrylate paste, mixed and prepared for polymerization, according to manufacturer's instructions. Two short-curing (11) and three long-curing cycles of polymerization (7), described in detail previously and summarized in Table 1 were used in the study.

Two g of specimen were scraped off each polymerized plate. Ten specimens were made for each material and for each procedure of polymerization. Thus prepared experimental specimens of PMMA powder and ground specimens were extracted by means of a polar solvent, methanol, for residual monomer to be demonstrated by a modified method of gas chromatography (10) on a Perkin Elmer device (Norwalk, Conn., USA), as described in detail elsewhere (11).

Results

Figures 1–2 and Tables 2–5 show results of residual monomer determination in all preparations of Biocryl R and Major Base R materials, their arithmetical means, standard deviations and coefficients of variation for particular subgroups of specimens. Evaluation of differences in arithmetical means of the variables studied was tested by Student's t-test, whereas significance was determined at the level of $p < 0.05$.

Table 2 shows a high percentage of residual monomer in PMMA powder Biocryl R (2.5%), whereas polymerized specimens of the same material revealed a significant decrease in the value of residual monomer. With this material, no significant differences in the residual monomer findings were observed among short-cycle cured subgroups of specimens.

Table 3 reveals that the Major Base R material also exhibited significantly lower values of residual monomer in the short-cycle cured specimens than in PMMA powder. A significantly lower value of residual monomer in the Major Base R PMMA powder as compared to the Bio-

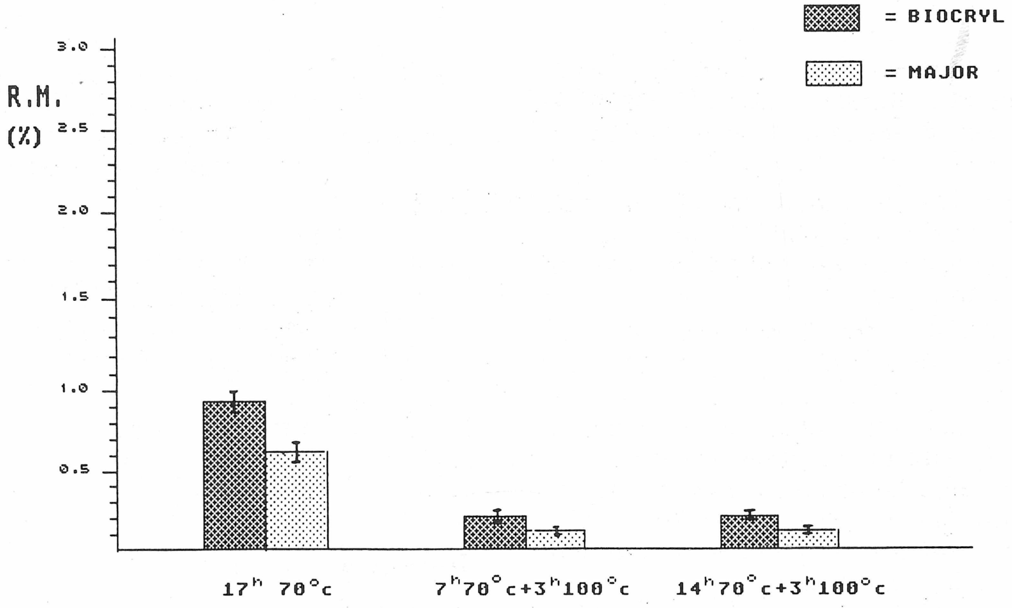

Fig. 2. *Histograms of the residual monomer levels for three long curing cycles of the materials under study*

Slika 2. *Histrogramski prikaz nalaza ostatnog monomera za tri dugotrajna polimerizacijska postupka istraživanih materijala.*

able 1. *Curing cycles chosen for the study*

ablica 1. *Polimerizacijski postupci, odabrani za istraživanje*

Curing cycle				
Short		Long		
Classical eterogeneous)	Presstherm (Bego)	1	2	3
30'70°C + 30'100°C	2,06 kPa 30'70°C + 30'100°C	14^{h}70°C	7^{h}70°C + 3^{h}100°C	14^{h}70°C + 3^{h}100°C

able 2. *The residual monomer levels (%) for PMMA-powder and two short curing cycles of Biocryl R*

ablica 2. *Nalaz ostatnog monomera (%) za PMMA--prašak i dva kratkotrajna polimerizacijska postupka (Biocryl R)*

IOCRYL *R.M. (%)*

	PMMA-powder N=6	polymerised specimens	
		classical N=10	Presstherm N=10
$\bar{x}$	2,5	2,2	2,2
S D	0,2	0,1	0,2
C V	8,0	4,5	9,1

yl R PMMA powder was compared, which
so held true when results obtained for materials
short-cycle cured subgroups of specimens were
mpared.

As differentiated from the Biocryl R material,
ithmetical means were found to differ signifi-
ntly among the subgroups of short-cured Major
ase R materials.

In Tables 4 and 5, a significant residual mono-
er decrease with a prolonged cycle of poly-
erization is shown, however, the amount of
sidual monomer was reduced to an extremly
w level only with the addition of polymeriza-
n at 100°C. With three long-curing cycles, dif-
rences consistent with the results for PMMA
wder and for short-curing cycles were obser-
d among various materials.

Figures 1 and 2 illustrate the decrease in the
lue of residual monomer findings with the in-
oduction and prolongation of polymerization,
well as differences related to the material.

Table 3. *The residual monomer levels (%) for PMMA--powder and two short curing cycles of Major Base R*

Tablica 3. *Nalaz ostatnog monomera (%) za PMMA--prašak i dva kratkotrajna polimerizacijska postupka (Major Base R)*

MAJOR *R.M. (%)*

	PMMA-powder N=6	polymerised specimens	
		classical N=10	Presstherm N=10
$\bar{x}$	1,9	1,5	1,2
S D	0,1	0,2	0,3
C V	5,3	13,3	2,5

Table 4. *The residual monomer levels (%) for three different long curing cycles of Biocryl R*

Tablica 4. *Nalaz ostatnog monomera (%) za tri dugotrajna polimerizacijska postupka (Biocryl R)*

BIOCRYL *R.M. (%)*

	polymerised specimens		
	14^{h}70°C N=10	7^{h}70°C+3^{h}100°C N=10	14^{h}70°C+3^{h}100°C N=10
$\bar{x}$	0,9	0,2	0,2
S D	0,08	0,02	0,01
C V	8,9	10,0	5,0

Table 5. *The residual monomer levels (%) for three different long curing cycles of Major Base R*

Tablica 5. *Nalaz ostatnog monomera (%) za tri dugotrajna polimerizacijska postupka (Major base R)*

MAJOR *R.M. (%)*

	polymerised specimens		
	14^{h}70°C N=10	7^{h}70°C+3^{h}100°C N=10	14^{h}70°C+3^{h}100°C N=10
$\bar{x}$	0,6	0,1	0,1
S D	0,05	0,01	0,009
C V	8,3	10,0	9,0

Discussion

A high value of residual monomer in PMMA powder is characteristic of the suspension polymerization cycle during the procedure of manufacture. A portion of this monomer is evidently polymerized during denture base manufacturing, depending on the polymerization cycle used. Thus, taking into account the results obtained and notable differences among PMMA powders of the materials under study as well as other relevant factors, a PMMA powder containing the lowest amount of residual monomer should be chosen when short-curing cycles are applied.

In polymerisates obtained by short-curing cycles, the level of residual monomer is about 10-fold that found in those submitted to long-curing cycles. Results of this study are consistent with those previously reported (6, 13). Denture bases polymerized by short-curing cycles are likely to cause a reaction of oral mucosa much earlier than those polymerized by long-curing cycles.

In keeping with own experience and previous investigations, most short-curing cycles are manually controlled by a dental technician, which may cause variations in the cycle duration and temperature (6). Short-curing cycles are most popular for various practical reasons. Therefore, instructions provided by manufacturers of denture base resins should be strictly followed and the cycles of polymerization performed on currently used instruments with automated control of duration, temperature and pressure. All this, along with the short-curing cycles chosen, should be considered when interpreting certain differences in the findings of residual monomer among particular specimen subgroups. Previous studies have clearly shown that during long-curing cycles, when polymerization at 100°C during at least 1 h is included, almost a complete conversion of MMA occurs. Results of this study confirmed the long-curing cycles without an interval at 100°C to be inadequate. Thus polymerized denture bases have a significantly higher level of residual monomer which is still within the risky amount. Therefore, a high-quality cycle of polymerization during 7 h at 70°C supplemented with additional 3 h at 100°C (for at least 1 h) is recommended (6–9, 13). Prolongation of the cycle does not result in any practical or statisticaly significant reduction of residual monomer, thus it appears to be quite unnecessary. Possible minor differences among the materials of different manufactures are of academic importance only.

Differences in the behavior of the materials under study observed during particular cycles of polymerization pointed to the need of further investigation including a greater number of PMMA products, different batches of the same product with special reference to the components of PMMA powder and PMMA liquid, and other relevant factors.

Conclusions

1. The two PMMA powders under study had a high although statistically significantly different percentage of residual monomer.

2. The values of residual monomer were significantly lower in polymerized specimens than in the respective PMMA powders.

3. The material with a lower value of residual monomer in PMMA powder also showed a consistently significantly lower value of residual monomer in polymerized specimens.

4. The values of residual monomer in the specimens obtained by short-curing cycles were still too high and risky for oral mucosa.

In case that short-curing cycles have to be employed for various practical reasons, automated control of polymerization should be provided, manufacturer's instructions followed, and methylmethacrylate resins with lower values of residual monomer in PMMA powder used.

5. High-quality cycles are time-consuming, obligatorily including polymerization at 100°C. A cycle taking 7 h at 70°C and 3 at 100°C, resulting in practically negligible amounts of residual monomer, is thus recommended.

ULOGA OSTATNOG MONOMERA PMMA-PRAŠKA I METODE POLIMERIZACIJE U NALAZU OSTATNOG MONOMERA POLIMETILMETAKRILATNE PROTEZNE BAZE

Sažetak

Količina ostatnog monomera u metilmetakrilatnim smolama za baze proteze izravno je ovisna o izboru polimerizacijskog postupka. Ostatni monomer u PMMA-prašku nije još dovoljno istražen. Svrha istraživanja bila je odrediti količinu ostatnog monomera u nekim PMMA-prašcima, korištenim za bazu proteze. Istraživanje je obuhvatilo mjerenje količine ostatnog monomera u pripravcima, polimeriziranim različitim polimerizacijskim metodama, s namjerom da se provjeri međuovisnost nalaza ostatnog monomera PMMA-praška i pripadajuće skupine toplopolimeriziranih pripravaka smole.

U istraživanju su korišteni materijali iz skupine polimetilmetakrilatnih smola tipa I, klasa 1. (1. »Biocryl R«, »Galenika«, Beograd – Zemun; 2. »Major base R«, »Major Dental Industry«, Torino). Eksperimentalni pripravci razvrstani su u dvije skupine: 1. originalni PMMA-prašci; 2. polimerizirani pripravci, dobiveni pomoću dvije metode kratkotrajne polimerizacije (a) frakciona, klasična, heterogena; b) aparatom »Prestherm«, »Bego«), te tri dugovremene (a) 14h na 70°C; b) 7h na 70°C i 3h na 100°C; c) 14h na 70°C i 3h na 100°C). Po 2 gr praška/izbruska ekstrahirano je metanolom u svrhu dokazivanja ostatnog monomera modificiranom metodom plinske kromatografije u aparatu »Perkin Elmer Co.« (Norwalk, Conn., SAD).

Originalni PMMA-prašci imaju visoki postotak ostatnog monomera, iako znatno različit. U polimeriziranim pripravcima ostatni monomer je znatno nižih vrijednosti negoli u odnosnim PMMA-prašcima. Kratkotrajni polimerizacijski postupci ostavljaju razmjerno mnogo ostatnog monomera, iako manje kada originalni PMMA-prašak ima nižu vrijednost slobodnog monomera, što može imati praktično značenje. Preporučuje se postupak polimerizacije trajanja 7h na 70°C i 3h na 100°C, koji rezultira zanemarivim količinama ostatnog monomera.

Ključne riječi: *ostatni monomer, PMMA-prašak, kratkotrajna polimerizacija, dugovremena polimerizacija, plinska kromatografija*

Adresa autora:
Address for correspondence:

Vjekoslav Jerolimov
Department of Removable
Prosthodontisc, Zagreb
University School
of Dentistry, Zagreb
Gundulićeva 5

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