Original Article

Residual Monomer of Autopolymerized Acrylic Resin According to Different Manipulation and Polishing Methods

An In Situ Evaluation

Tatiana Siqueira Gonçalves[a]; Luciane Macedo de Menezes[b]; Luiz Ernani Aguiar Silva[c]

ABSTRACT

Objective: To test the hypothesis that no difference exists in the in situ levels of residual monomer of an autopolymerized acrylic resin, irrespective of the method of manipulation and polishing.

Materials and Methods: Forty volunteers received the test specimens. The residual monomer was evaluated by means of gas chromatography using methylethylketone as extraction solvent. The samples of autopolymerized acrylic resin were submitted to two methods of manipulation—mass and addition—as well as to two types of polishing—mechanical and chemical. Four test groups were determined according to manipulation and polishing techniques: mass-mechanical; mass-chemical; addition-mechanical; addition–chemical. The data obtained were analyzed by the Student's *t*-test for paired samples as well as by analysis of variance.

Results: Residual methylmethacrylate was verified in high concentrations in the beginning of the testing as well as 24 hours after the test specimens had been worn. Mechanical polishing was associated with lower levels of residual monomer. The mass-mechanical group showed the lowest values. Mechanical polishing was associated with the lowest levels of residual monomer, and the lowest level of all occurred in mass-mechanical group.

Conclusions: The hypothesis is rejected. Variations of residual polymer were associated with variations in the manipulation and polishing, but high concentrations of residual monomer were present in all groups. These concentrations were reduced after 24 hours.

KEY WORDS: Residual monomer; Acrylic resins; Removable appliances

INTRODUCTION

Dentistry has used polymethylmetacrylate acrylic (PMMA) resins since the mid-20th century.[1] These materials originate from ethylene and are high molecular weigh polymers that polymerize in an addition reaction, with no residual products. Although the curing process can also be initiated by heat or light, a chemical initiator is more often used.[2]

In orthodontics, PMMA resins are extremely important because they can be used to build up removable or auxiliary fixed appliances as well as retainers. There are different possibilities for manipulating and polishing this material. For manipulation, two techniques are described: the addition technique (or salt and pepper), in which the polymer is saturated by its monomer, is widely used in orthodontics; and the mass technique, also a cold-cured technique, in which powder and liquid are mixed together,[3] is commonly used in prosthodontics. After polymerization, PMMA appliances are ground and polished.[3] Polishing can be carried out through mechanical devices[2,4] (mechanical polishing) or chemical products (chemical polishing), which consists of immersing the acrylic appliance in heated, chemical, polishing liquids.[5]

Some orthodontic appliances can be used for many months and kept in contact with the oral mucosa for a long period, so the methylmetacrylate's (MMA) biolog-

---

[a] Postgraduate (MS), Department of Orthodontics, Pontifical Catholic University of Rio Grande do Sul, Rio Grande do Sul, Brazil.

[b] Professor, Department of Orthodontics, Pontifical Catholic University of Rio Grande do Sul, Rio Grande do Sul, Brazil.

[c] Professor, Department of Chemistry, Pontifical Catholic University of Rio Grande do Sul, Rio Grande do Sul, Brazil.

Corresponding author: Ms Tatiana Siqueira Gonçalves, Department of Orthodontics, Pontifical Catholic University of Rio Grande do Sul, Av. Ipiranga, 6681—Prédio 6, Sala 209, Porto Alegre, Rio Grande do Sul, Brazil
(e-mail: tatianasgoncalves@terra.com.br)

Accepted: September 2007. Submitted: June 2007.

DOI: 10.2319/060407-265.1

ical effects must be considered. In this way, residual monomer of acrylic resins and its dilution have been widely investigated,[6–19] indicating the presence of unreacted residual monomer during the first 24 hours after polymerization.[11,12,16,20,21] MMA is considered an allergen[22–25] and can cause local adverse reactions, such as erythema, a burning sensation, edema, fissures, necrosis, pain,[13,25,26] and it can even cause some systemic reactions.[27] such as labial edema,[25] chronic urticaria,[28] difficulty in swallowing, and hypersalivation.[29] MMA is also considered cytotoxic[18,30–35] as well as possibly genotoxic.[36,37]

This study was developed to test the manipulation and polishing techniques influence the level of the residual monomer, which, in turn, affects the biocompatibility of this material. The aim of this study was to evaluate, in situ, the effect of two manipulation and two polishing techniques on the residual monomer of an autopolymerized acrylic resin.

MATERIALS AND METHODS

An MMA autopolymerized acrylic resin (JET, Clássico, São Paulo, Brazil) was analyzed for this study. Its liquid contains 98% MMA monomer and dimethyl-p-toluidine, and the powder contains PMMA, ethyl acrylate and benzoyl peroxide. For this in situ study, 40 volunteers took part on the investigation, signing an agreement form. This investigation was also approved by the ethical committee of the Pontifical Catholic University of Rio Grande do Sul.

An impression of the maxillary arch of each volunteer was taken. Cast models were obtained to construct an autopolymerized acrylic resin appliance, with no clasps, for each subject. The samples were placed in this appliance, which kept them in contact with saliva. During the appliance's curing process, a metallic matrix (16 mm × 13 mm × 3 mm) (Figure 1A) was placed over the resin (Figure 1B), creating a depression on the appliance, so that samples could be placed (Figure 2) and any damage to the volunteers could be avoided.

Four experimental groups were established. Each one had 10 volunteers. For each volunteer, two samples of a group were produced, so that each experimental group had 20 samples: 10 for the initial residual monomer analysis and 10 for analysis at 24 hours, totaling 80 samples, according to Table 1.

To obtain the samples, a metallic matrix (5 mm × 5 mm × 2 mm) was impressed with silicon (Figure 3A). This impression (Figure 3B) was filled with acrylic resin. Powder was weighed (AG204, Metler Toledo, Switzerland), and the liquid was measured with a microsyringe (Lab Mate, PZ HTL SA, Warsaw, Poland). For the mass manipulation technique mass, 0.250 g of

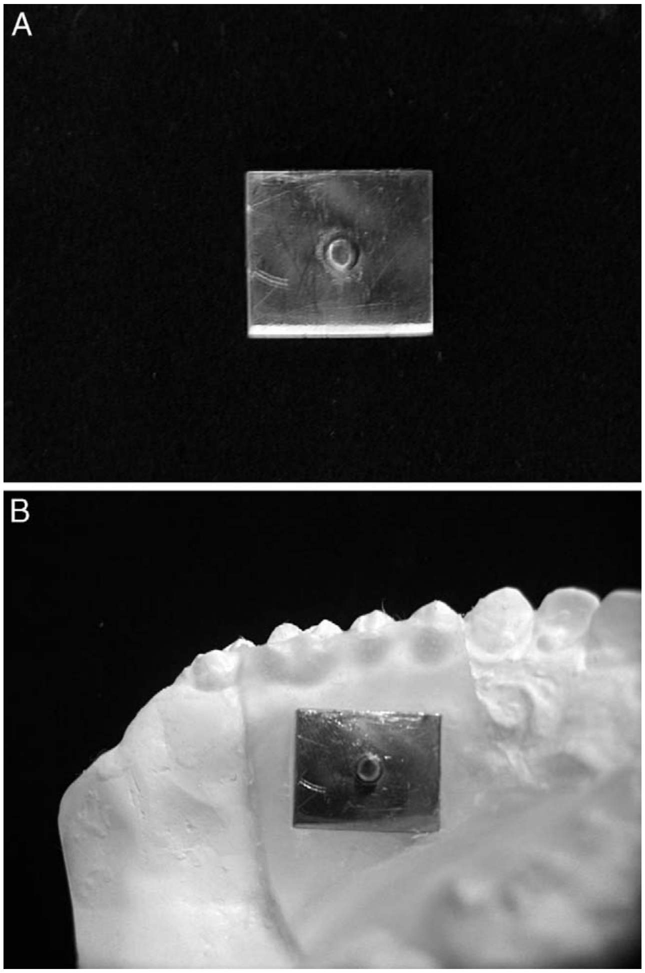

Figure 1. (A) Metallic matrix. (B) Impression of metallic matrix over the acrylic removable appliance.

Figure 2. Acrylic appliance used by the volunteers.

Table 1. Distribution of samples according to manipulation and polishing techniques, experimental group and evaluations

				Distribution of Samples	
Manipulation	Polishing	Experimental Group	No. of Volunteers	Initial Residual Monomer	24-hour Residual Monomer
Mass	Mechanical	Mechanical-Mass	10	10	10
	Chemical	Mechanical-Chemical	10	10	10
Addition	Mechanical	Addition-Mechanical	10	10	10
	Chemical	Addition-Chemical	10	10	10
Total			40	40	40
				80	

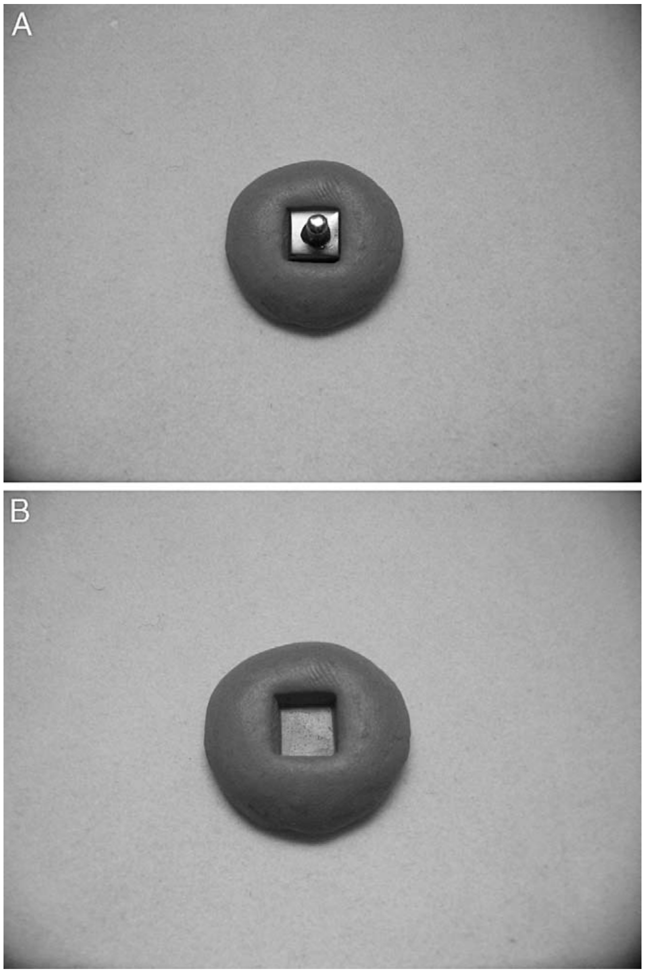

Figure 3. (A) Silicon impression of the metallic matrix. (B) Silicon mold.

polymer and 100 μL of monomer were mixed together, and the resin was poured into the two molds. For the addition technique, 0.125 g of polymer and 50 μL of monomer were gradually poured into each of the two impressions, for the samples to weigh approximately 0.1 g following the manufacturer's instructions. After 20 minutes, the samples were ground with a tungsten bur and abrasive paper (No. 400 and No. 600), and polishing begun.

For mechanical polishing, a black brush and felt wheel with pumice slurry were used. After that, a soft wheel was applied with chalk powder. Each instrument was applied 10 times for 2 seconds, and instruments were discarded after polishing 15 samples. In the chemical polishing groups, samples were drowned into the chemical polisher (PQ-9000, Termotron, São Paulo, Brazil), containing 20 mL of chemical polishing liquid (Poli Quim, Clássico, São Paulo, Brazil) at 70°C. This liquid is basically composed of MMA monomer, but some stabilizers are also added to the formula. The samples were left to bench-dry until visible excessive monomer could evaporate, which took about 30 minutes.

After that, two samples were placed on the acrylic appliance of each volunteer: one for the initial analysis and the other for the 24-hour residual monomer analysis. To intentionally wait for the highest levels of residual monomer to fall, the appliance was not delivered to the volunteer for 18 hours. Just before the appliances were delivered to the volunteers, they were told to wear the appliance at all times, except for meals and during oral hygiene, reproducing the clinical situation. Also, basic information on how to store (in an appropriate plastic box) and clean the appliance (with cold water and dental brush) was given.

Immediately before the appliances were delivered, the initial samples were collected, and each sample was added to an identified glass tube containing 2.5 mL of methylethylketone (PA 99%, Quimex, Merck S.A., São Paulo, Brazil). This tube was sealed with a cork cap and stored in a dark place at 4°C for 48 hours. The same procedure was repeated for the 24 hour samples.

After 48 hours of storage, the tubes were centrifuged at 2000 rpm for 15 minutes and 1 μL of the supernatant was removed with a microsyringe, which was immediately injected in a chromatographer. The equipment used was a gas chromatographer Auto System XL (Perkin Elmer, Warthan, MA), equipped with a ZB-WAX (Zebron, Torrance, CA) column, 30 m long and 0.25 mm cross section, using polyethylene glycol as stationary phase and nitrogen as carrier gas. The equipment was calibrated with different concen-

Table 2. Comparison of Initial and 24 hours' residual monomer percentiles for each evaluated group

Comparison	No.	Mean (%)	Standard Deviation (%)	*P*
Mass-Mechanical				
Initial	10	4.81	0.67	.01*
24 hour	10	3.60	1.25	
Mass-Chemical				
Initial	10	6.79	0.89	.02*
24 hour	10	5.04	1.54	
Addition-Mechanical				
Initial	10	5.02	1.07	.01*
24 hour	10	3.79	1.67	
Addition-Chemical				
Initial	10	5.47	1.63	.03*
24 hour	10	3.84	1.77	

* Statistical difference.

Table 3. Comparison of residual monomer percentiles between groups in both analyzed periods

Comparison	No.	Mean (%)	Standard Deviation (%)	*P*
Initial				
Mass-Mechanical	10	4.81[A**]	0.67	
Mass-Chemical	10	6.79[B**]	0.89	.01*
Addition-Mechanical	10	5.02[A**]	1.07	
Addition-Chemical	10	5.47[AB**]	1.63	
24 hour				
Mass-Mechanical	10	3.60	1.25	
Mass-Chemical	10	5.04	1.54	.17
Addition-Mechanical	10	3.79	1.67	
Addition-Chemical	10	3.84	1.77	

* Statistical difference.

** Means followed by the same letter show no statistical difference.

trations of a 99% pure grade MMA solution (Merck-Schuchardt, Darmstadt, Germany) to build a calibration curve, which was used to calculate the concentrations in the samples and as a control.

RESULTS

The Student's *t*-test for paired samples (Table 2) showed statistical difference for residual monomer between the initial and 24-hour results for all comparisons. In 24 hours, the percentages were reduced. Analysis of variance (Table 3) showed statistical difference between the groups only for the initial analysis. Also, the mass-chemical group showed the highest average value, followed by the addition-chemical group (which did not differ from mass-chemical). With lower average values, the addition-mechanical and mass-mechanical groups did not differ from each other or from the addition-chemical group ($P = .01$).

DISCUSSION

This study results showed that there was residual monomer in the acrylic resin evaluated (Table 2). Independent of the activation method, the literature shows the presence of residual monomer.[6–19,31,33] Residual monomer concentrations were high, especially for the initial samples. Once residual monomer is linked to hypersensitivity and allergic reactions, it should be as low as possible. The residual monomer of autopolymerized acrylic resins should not exceed 3.5%.[9] According to this standard, none of the applied techniques would be approved, although the mass-mechanical group almost achieved this level in 24 hours.

Yilmaz et al[38] cited the ISO 1567, which established that 4.5% would be an acceptable limit for residual monomer for this kind of resin. This value is near the one found for mass-mechanical group (Table 2). Stafford and Brooks,[16] who also tested the salt-and-pepper technique, registered average values of residual monomer of an orthodontic autopolymerized acrylic resin and found levels between 1.49% and 4.51%. Valittu[19] verified residual monomer between 4.8% and 6.9%, which is similar to the levels found in this study, whereas Kedjarune et al [31] had results between 1.88% and 4.32%, and Davy and Braden[8] found levels between 0.045% and 0.18%; these findings were much lower than the ones found here.

Although all of these researchers studied autopolymerized acrylic resin, the wide variety of results for this kind of analysis is certainly linked to methodologic diversity, considering not only the different polymerization cycles but also the residual monomer extraction method. In the current study, gas chromatography was used, which was previously used by other authors,[6,13–15,17,31,38] reproducing the method suggested by Sadamori et al.[15]

The greatest drop in residual monomer concentrations usually occurs during the first 24 hours of use, and the major dilution also occurs mainly in the first 24 hours.[7,11,16,20,21] This was confirmed by the current investigation. It has been suggested[12] that two mechanisms would be responsible for this 24-hour reduction: late conversion of residual monomer into polymer, once there are free radicals that remain on the piece after curing, and diffusion of monomer out of the acrylic appliance.

At first, one of the aims of this study was to verify residual monomer not only in 24 hours, but also after 7 and 20 days of use by the volunteers, in order to have a more longitudinal study. However, during the investigation, the chromatographer's column was contaminated by the samples, probably because of biofilm and salivary enzymes, which did not allow readings for these periods; this same situation occurred in other studies.[7,10]

Chemical polishing has an advantage because it is not time consuming,[5,21] but it seems to have some effect on the resin's physical properties. Braun et al[20] tested residual monomer of auto- and thermopolymerized acrylic resin with mechanical and chemical polishing, which caused the highest levels of residual monomer for both kinds of resin in all studied periods. Also, Nunes de Mello et al[21] reported the highest values of residual monomer with chemical polishing. The same was observed here, where mechanical polishing led to the lowest levels of residual monomer and chemical polishing led to the highest.

Today there are some sealants that substitute polishing, which are UV-light activated. These materials, as well as chemical polishers, are not time consuming to use. Valittu[19] evaluated the effect of different surface treatments on residual monomer and found that these sealants led to reduced levels of residual monomer, probably because of an increase in temperature during its curing cycle. These sealants were not investigated here, but they seem to be an advantageous alternative and potentially interesting to investigators.

Some studies have assessed the biocompatibility of autopolymerized acrylic resins.[18,30–35] It has been shown that this material is cytotoxic. In this way, it has been stated that the longer a resin is left to elute its toxic components, the lower the cytotoxic effect exerted.[35] In addition, some studies have tried to access the genotoxicity of acrylic resins,[36,37] but more studies should be developed in this field for autopolymerized acrylic resins.

Clinically, all efforts should be made to have low levels of residual monomer in order to reduce the occurrence of undesired reactions to this material. It has been shown that the right proportions of powder and liquid reduce residual monomer.[12,31] Polymerization in water or under pressure is also a way to try to reduce levels of residual monomer,[12,39,40] as well as additional polymerization cycles.[13,21,40,41] Besides that, maneuvers can be done to reduce residual monomer after the appliance is already finished: hot water storage for at least 1 hour after construction, water immersion for 24, 36, or even 72 hours before delivery,[16,18,24,31,33] which is in accordance with the findings of the present study and, as proposed by Valittu[19] and as seen in this study, adequately using mechanical polishing. These approaches can be taken to try to reduce the frequency of allergic and hypersensitivity reactions.

CONCLUSIONS

- The different manipulation and polishing techniques used resulted in different levels of residual monomer.
- All of the methods used showed high levels of residual monomer. The percentages of residual monomer were reduced after 24 hours.

REFERENCES

1. Peyton FA. History of resins in dentistry. *Dent Clin North Am.* 1975;19:211–222.
2. Anusavice KJ. *Phllip's Science of Dental Materials.* Philadelphia, PA: WB Saunders; 1996:211–271.
3. Adams CP. *Aparelhos ortodônticos removíveis.* São Paulo, Brazil: Santos; 1987:241–244.
4. Ulusoy M, Ulusoy N, Aydin AK. An evaluation of polishing techniques on surface roughness of acrylic resins. *J Prosthet Dent.* 1986;56:107–112.
5. Gotusso MJ. [Chemical surface treatment of acrylic resins]. *Rev Asoc Odontol Argent.* 1969;57:359–361.
6. Austin AT, Basker RM. The level of residual monomer in acrylic denture base materials with particular reference to a modified method of analysis. *Br Dent J.* 1980;149:281–286.
7. 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;67:1295–1299.
8. Davy KW, Braden M. Residual monomer in acrylic polymers. *Biomaterials.* 1991;12:540–544.
9. Harrison A, Huggett R. Effect of the curing cycle on residual monomer levels of acrylic resin denture base polymers. *J Dent.* 1992;20:370–374.
10. Koda T, Tsuchiya H, Yamauchi M, Ohtani S, Takagi N, Kawano J. Leachability of denture-base acrylic resins in artificial saliva. *Dent Mater.* 1990;6:13–16.
11. Lamb DJ, Ellis B, Priestley D. Loss into water of residual monomer from autopolymerizing dental acrylic resin. *Biomaterials.* 1982;3:155–159.
12. Lamb DJ, Ellis B, Priestley D. The effects of process variables on levels of residual monomer in autopolymerizing dental acrylic resin. *J Dent.* 1983;11:80–88.
13. 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;140:347–350.
14. Sadamori S, Kotani H, Hamada T. The usage period of dentures and their residual monomer contents. *J Prosthet Dent.* 1992;68:374–376.
15. Sadamori S, Shigeto N, Hamada T, Okuda K. A method of determining residual monomer in acrylic resin using methyl ethyl ketone. *Aust Dent J.* 1990;35:509–513.
16. Stafford GD, Brooks SC. The loss of residual monomer from acrylic orthodontic resins. *Dent Mater.* 1985;1:135–138.
17. Sadamori S, Ganefiyanti T, Hamada T, Arima T. Influence of thickness and location on the residual monomer content of denture base cured by three processing methods. *J Prosthet Dent.* 1994;72:19–22.
18. Tsuchiya H, Hoshino Y, Tajima K, Takagi N. Leaching and cytotoxicity of formaldehyde and methyl methacrylate from acrylic resin denture base materials. *J Prosthet Dent.* 1994; 71:618–624.
19. 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;54:188–192.
20. Braun KO, Mello JA, Rached RN, Del Bel Cury AA. Surface texture and some properties of acrylic resins submitted to chemical polishing. *J Oral Rehabil.* 2003;30:91–98.
21. Nunes de Mello JA, Braun KO, Rached RN, Del Bel Cury AA. Reducing the negative effects of chemical polishing in

acrylic resins by use of an additional cycle of polymerization. *J Prosthet Dent.* 2003;89:598–602.

22. Auzerie V, Mahe E, Marck Y, Auffret N, Descamps V, Crickx B. Oral lichenoid eruption due to methacrylate allergy. *Contact Dermatitis.* 2001;45:241.
23. Fernstrom AI, Oquist G. Location of the allergenic monomer in warm-polymerized acrylic dentures. Part I: Causes of denture sore mouth, incidence of allergy, different allergens and test methods on suspicion of allergy to denture material—a survey of the literature. Case report, allergenic analysis of denture and test casting. *Swed Dent J.* 1980;4:241–252.
24. Giunta J, Zablotsky N. Allergic stomatitis caused by self-polymerizing resin. *Oral Surg Oral Med Oral Pathol.* 1976; 41:631–637.
25. Ruiz-Genao DP, Moreno de Vega MJ, Sanchez Perez J, Garcia-Diez A. Labial edema due to an acrylic dental prosthesis. *Contact Dermatitis.* 2003;48:273–274.
26. Stungis TE, Fink JN. Hypersensitivity to acrylic resin. *J Prosthet Dent.* 1969;22:425–428.
27. Morris-Jones R, Robertson SJ, Ross JS, White IR, McFadden JP, Rycroft RJ. Dermatitis caused by physical irritants. *Br J Dermatol.* 2002;147:270–275.
28. Lunder T, Rogl-Butina M. Chronic urticaria from an acrylic dental prosthesis. *Contact Dermatitis.* 2000;43:232–233.
29. Goncalves TS, Morganti MA, Campos LC, Rizzatto SM, Menezes LM. Allergy to auto-polymerized acrylic resin in an orthodontic patient. *Am J Orthod Dentofacial Orthop.* 2006; 129:431–435.
30. Huang FM, Tai KW, Hu CC, Chang YC. Cytotoxic effects of denture base materials on a permanent human oral epithelial cell line and on primary human oral fibroblasts in vitro. *Int J Prosthodont.* 2001;14:439–443.
31. Kedjarune U, Charoenworaluk 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.
32. Lai YL, Chen YT, Lee SY, Shieh TM, Hung SL. Cytotoxic effects of dental resin liquids on primary gingival fibroblasts and periodontal ligament cells in vitro. *J Oral Rehabil.* 2004; 31:1165–1172.
33. Rose EC, Bumann J, Jonas IE, Kappert HF. Contribution to the biological assessment of orthodontic acrylic materials. Measurement of their residual monomer output and cytotoxicity. *J Orofac Orthop.* 2000;61:246–257.
34. Schuster GS, Lefebvre CA, Dirksen TR, Knoernschild KL, Caughman GB. Relationships between denture base resin cytotoxicity and cell lipid metabolism. *Int J Prosthodont.* 1995;8:580–586.
35. Sheridan PJ, Koka S, Ewoldsen NO, Lefebvre CA, Lavin MT. Cytotoxicity of denture base resins. *Int J Prosthodont.* 1997;10:73–77.
36. Gigola P, Monarca S, Feretti D, Zerbini I, D'Argenio D. Evaluation of the clastogenic activity of some resins used in the prosthodontic field. *Minerva Stomatol.* 2001;50:361–371.
37. Schweikl H, Schmalz G, Spruss T. The induction of micronuclei in vitro by unpolymerized resin monomers. *J Dent Res.* 2001;80:1615–1620.
38. Yilmaz H, Aydin C, Caglar A, Yasar A. The effect of glass fiber reinforcement on the residual monomer content of two denture base resins. *Quintessence Int.* 2003;34:148–153.
39. Lee SY, Lai YL, Hsu TS. Influence of polymerization conditions on monomer elution and microhardness of autopolymerized polymethyl methacrylate resin. *Eur J Oral Sci.* 2002;110:179–183.
40. Yunus N, Harrison A, Huggett R. Effect of microwave irradiation on the flexural strength and residual monomer levels of an acrylic resin repair material. *J Oral Rehabil.* 1994;21: 641–648.
41. Koutis D, Freeman S. Allergic contact stomatitis caused by acrylic monomer in a denture. *Australas J Dermatol.* 2001; 42:203–206.