

Residual Acrylic Monomer Content of Denture Base Resins with Different Fiber Systems

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ABSTRACT: The conversion of monomer to its polymer may not be complete and residual monomer is left over in the polymeric matrix; this, in turn, affects the properties of the polymeric matrix. In this study, we wanted to compare residual monomer content of the unreinforced conventional heat-polymerized and microwave-polymerized acrylic resins with those of fiber-reinforced ones. High performance liquid chromatography was used for the determination of the residual monomer content. Statistical analysis of the results was carried out with a confidence level of 95%. It was observed that conventional heat-polymerized denture base resin resulted in a rela-

tively higher residual monomer content than the microwave one. Conventional heat-polymerized denture base resin with fiber reinforcement caused an increase in the residual monomer content. Furthermore, the change in the residual monomer content of microwave-polymerized denture base resin with fiber reinforcement was not statistically significant compared with no fiber reinforcement. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 471–476, 2012

Key words: dental polymers; high performance liquid chromatography; resins

INTRODUCTION

Poly(methyl methacrylate), PMMA, has been the most commonly used denture base material.^{1,2} The commercial denture base material package includes powder and liquid parts and the powder part contains PMMA, initiator (0.5–1.5% benzoyl peroxide), pigments (red HgS, yellow CdS, and/or brown Fe₂O₃), dyes, opacifier (TiO₂), and plasticizer (8–10% dibutyl phthalate or triphenylphosphate) and the liquid part contains monomer (MMA), inhibitor (0.003–0.1% hydroquinone), accelerator (for auto polymerized type, tertiary amines such as *N,N*-dimethyl-*p*-toluidine), plasticizer (butyl or acetyl methacrylate), and crosslinking agent (2–14% glycoldimethacrylate).³

Polymerization of methyl methacrylate (MMA) monomer can be initiated by chemical activation using component such as dimethyl-*p*-toluidine or decomposition of benzoyl peroxide with heat or microwave energy. It does not matter which polymerization method is employed; the conversion of the monomer to the polymer is usually not complete and this leaves some of the monomer units in the

polymer, namely, residual monomers.^{4–6} The residual monomer is a well-known plasticizer and affects the physical and mechanical properties of acrylic resins.^{7,8} Furthermore, the residual monomer units may diffuse from acrylic resin causing adverse effects, that is, redness, swelling, and pain on the oral mucosa.^{5,9,10} Infrared spectroscopy, gas chromatography, gas–liquid chromatography, and high performance liquid chromatography (HPLC) have been used to determine the content of residual monomer in polymeric matrices.^{4–9}

Adhesion between a polymer matrix and treated fiber is achieved by physical and chemical modifications.¹¹ The physical modification is the surface roughening of the fiber by the sputtering effect, in which an increase in the contact area and surface friction between fiber and the polymeric matrix occurs. In the chemical modification, active polar groups are introduced into the fiber surface and this decrease the surface energy and enhance chemical bonding between the fiber and the polymeric matrix.¹¹ Plasma treatment improves fiber-polymer matrix bonding by introducing polar or reactive groups or even with a new polymeric layer that is covalently bonded to the fiber.¹¹ However, the reinforced denture base materials show some disadvantages, such as higher cost, poor surface properties, difficulties with processing, possibility of occurrence of voids between the polymeric matrix and fiber.

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TABLE I
Dental Fiber Systems Used in This Study and the Fiber Content

Dental fiber	Fiber structure	Length (mm)	Fiber content (wt %) conventional	Fiber content (wt %) microwave	Fiber content (vol %) conventional	Fiber content (vol %) microwave
Stick	Continuous parallel e-glass	15	3.15	4.08	1.5	1.95
Stick Net	Woven e-glass	10	0.45	0.62	0.21	0.29
Ribbon	Woven polyethylene	15	0.39	1.41	0.48	1.72

Mechanical properties of unreinforced conventional heat-polymerized and microwave-polymerized denture base resin with those of denture base resin reinforced with continuous unidirectional e-glass, woven e-glass, and ultrahigh molecular weight polyethylene fibers have been compared in the previous study of the authors.¹² It was observed that reinforcement with continuous unidirectional e-glass fiber improved the mechanical properties.

Comparing the residual monomer (MMA) content of unreinforced conventional heat-polymerized and microwave-polymerized acrylic resins with those of acrylic resin reinforced with polyethylene fiber in woven form, e-glass fibers in continuous parallel (uni-directional) form, and e-glass fibers in woven (bi-directional) form was the purpose of this study. The hypothesis of the study was that the fiber reinforcement would increase the residual monomer content of the denture base materials. In addition, the results of the residual monomer content were related to the results of the previous study¹² on the mechanical properties of the denture base resins reinforced with different fibers.

MATERIALS AND METHODS

Two acrylic resins used in this study were heat-polymerized resins one was conventional heat-polymerized resin (Meliodent, Bayer Dental, Newbury, Berkshire, United Kingdom) and the other was microwave-polymerized resin (Acron MC, GC Dental, Tokyo, Japan). Microwave-polymerized denture base material (Acron MC) contains both powder (PMMA-ethylacrylate copolymer) and liquid (MMA, *N,N*-dimethyl-*p*-toluidine).¹³ Heat-polymerized denture base material (Meliodent) also contains both powder (PMMA, benzoyl peroxide as initiator) and liquid (MMA, ethylene glycol dimethacrylate).¹⁴ Dental fiber systems used for this study are given in Table I.

Specimen preparation for the determination of residual monomer content

For the determination of residual monomer content, five test specimens were prepared for each of eight groups of control (no fiber), continuous parallel

e-glass fiber, woven e-glass fiber, and woven polyethylene fiber reinforcing both of conventional heat- and microwave-polymerized denture base resins, that is, in total 40 samples were prepared for the residual monomer content test. Stainless steel molds with dimension of 20-mm diameter and 2-mm thickness were used to mold disk-shaped samples from the resins.

The powder-liquid ratios for the heat-polymerized resin and microwave-polymerized resin were 23.4 g/10 mL and 100 g/43 mL, respectively. Unreinforced conventional heat-polymerized specimens were prepared in conventional metal denture flasks and cured in a thermostatically controlled dry heat oven (Nüve EN500, Ankara, Turkey) for 1 h at 60°C and 2.5 h at 100°C, after 1 min of mixing and 6 min of doughing process at 23°C ± 2°C. Microwave-polymerized specimens were prepared in fiber-reinforced plastic flasks (FRP Flask, GC Industrial Corp, Tokyo, Japan) and microwave irradiated for 3 min at 500 W, after 15–20 min of doughing at 23°C ± 2°C. Before deflasking, all the specimens were bench-cooled. The samples prepared are shown in Figure 1.

For reinforced specimens, fibers were impregnated with powder/liquid mixture within a tin. Afterward, the wetted fibers were placed manually into the middle of the acrylic resin dough and pressed for 10 min in conventional metal denture flasks. Fiber contents, calculated based on weight and volume percentages, are given in Table I. The polymerization process was the same of the abovementioned polymerization process for the unreinforced test specimens.

Test specimens were wet-grounded with silicon carbide grinding papers of 200, 400, and 600-grit size with an automatic polishing machine (Grin PO 2V grinder-polisher, Metkon A.Ş., Bursa, Turkey). The residual monomer content was determined after storage of samples in distilled water at 37°C for 48 h. All of the samples were weighed accurately, placed in a round-bottomed glass flask and 50 mL of methanol, the extraction solvent, was added. Glass flasks, including specimen and methanol, were connected to the Soxhlet extractor and placed in a water bath, whose temperature was adjusted to the temperature range of 60–70°C, considering the

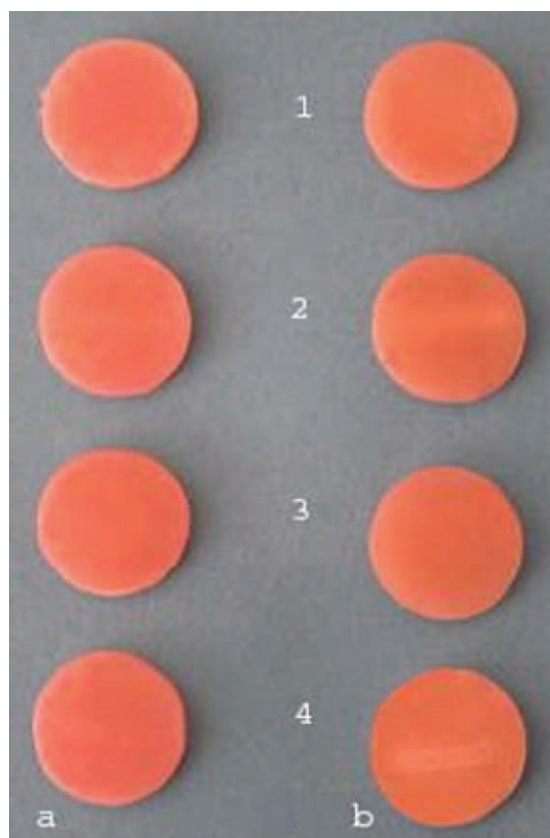


Figure 1 Samples prepared for the residual monomer content tests (a) conventional heat polymerized, (b) microwave polymerized (1-control, 2-continuous parallel e-glass fiber, 3-woven e-glass fiber, 4-crosslinked stitch woven polyethylene fiber). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

boiling point of methanol that is 64.5°C. Glass flasks, including sample and methanol, were kept in the water bath for 6 h, to remove the residual monomer from the sample.

Determination of residual methyl methacrylate monomer content

High performance liquid chromatograph (Agilent 1100 System, Woldbronn, Germany) was used to determine the residual monomer content. Analysis was performed using Agilent UV detector at 254 nm, Ace 5 C18 column, binary pump, and auto injector systems. Methanol-water isocratic mixture (70 : 30) was used as the mobile phase. Column temperature, pump flow rate, and injection volume were 25°C, 1 mL/min, and 2 μ L, respectively. One percent standard stock solutions of monomers were prepared by dissolving the monomer in methanol, and varied concentrations of these stock solutions were injected into the HPLC system. In this manner, standard peaks of monomer were obtained, peak areas were recorded, and these areas were measured for obtaining calibration curve. The calibration curve

was constructed by using the standard monomer peak area and the concentration of standards as shown in Figure 2.

Two micro liters of extract solution was injected each time via auto injector system and residual monomer peak areas were taken for each specimen solution by using standard solution peak height and time localization. Subsequently, residual monomer fraction (v/v%) for each extract was determined according to the calibration curve. Weight fractions of residual monomers were calculated for each sample. A validation study was not carried out for HPLC methodology.

Statistical analysis

The mean values and the standard deviations of residual monomer amounts for each group were calculated to compare the reinforced specimen groups with each other and with the specimens without fiber reinforcement. Analysis of variance and Duncan tests were applied for the statistical analysis. Statistical analysis of the tests results was carried out with a 95% confidence level.

RESULTS AND DISCUSSION

The calculated means and standard deviations of the residual monomer contents of test specimens are given in Figure 3.

A relatively higher amount of residual monomer content was extracted from the heat-polymerized denture base material than that of microwave-polymerized denture base material for both of reinforced and nonreinforced cases. All fiber reinforcements did not change the residual monomer content for microwave-polymerized acrylic resin ($P > 0.05$). The content of residual monomer for heat-polymerized acrylic resins was ranked as; woven e-glass fiber > continuous parallel e-glass fiber > woven polyethylene fiber > control. Residual monomer content of heat-polymerized acrylic resin with fiber reinforcement was higher than the upper limit of residual monomer content (2.2 wt %) set by the ISO 1567.

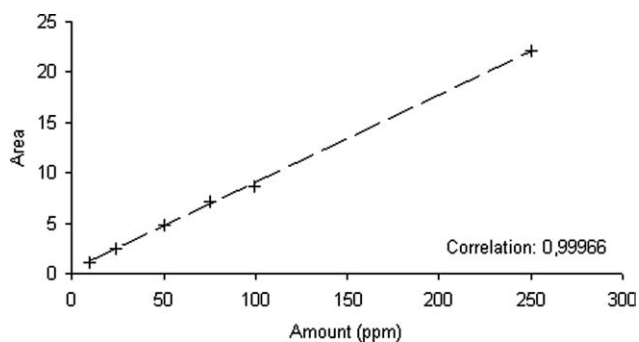


Figure 2 Calibration curve.

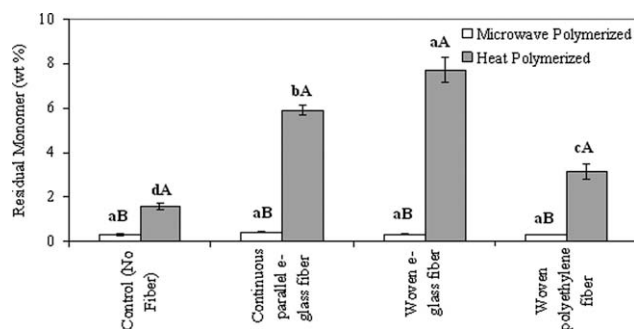


Figure 3 Mean values of residual monomer (wt %) test specimens. [Different upper case letters mean statistically significant difference ($P < 0.05$) between acrylic resins within each fiber group; different lower case letters mean statistically significant difference ($P < 0.05$) among fiber groups for each acrylic resin].

On the other hand, residual monomer content of microwave-polymerized acrylic resin with fiber reinforcement was lower than the upper limit of residual monomer content.

Woven e-glass fiber reinforcement in conventional heat-polymerized denture base material has the highest level of residual monomer content. The statistical analysis showed that the difference between the mean values of residual monomer content was statistically significant ($P < 0.05$) regarding the resin type for all fiber groups. The difference between the mean values of residual monomer content was statistically significant ($P < 0.05$) for each control, continuous parallel e-glass fiber, woven e-glass fiber, and woven polyethylene fiber groups of conventional heat-polymerized resin regarding fiber type, whereas this was not the case for the microwave-polymerized resin. The increase in the residual monomer content of conventional heat-polymerized denture base material reinforced with fiber could be ascribed to (a) different content of the resins, (b) mode of heat transfer, and (c) oxygen inhibition.

Regarding the different content of the denture base resin materials, *N,N*-dimethyl-*p*-toluidine is used as the accelerator in the microwave-polymerized case and the polymerization reaction is very fast compared with that of conventional heat polymerization. The amount of residual monomer content is relatively lower in the microwave-polymerized case probably due to the higher reaction rate and internal heat produced during microwave irradiation. Benzoyl peroxide is used as the initiator that forms the free radicals for the polymerization reaction, and ethylene glycol dimethacrylate is used as crosslinking agent for the conventional heat-polymerized denture base resin. Initiator's efficiency is very important factor for the polymerization reaction. Side reactions and nonhomolytic cleavage of the initiator decrease the rate of

conversion of monomer to polymer during the polymerization reaction. In other words, decrease in the efficiency of the radical initiator increases the residual monomer content.

Regarding the mode of heat transfer, microwave heating of denture base resins might probably provide rather a uniform heat transfer throughout the matter compared with conductive heat transfer. MMA could be polymerized via microwave energy due to polarity of MMA, and microwave irradiation allows the MMA molecules to orient themselves at a frequency of 2450 MHz, and polarized molecules are flipped over rapidly while generating heat due to molecular friction.¹⁵ In the conventional heat polymerization, monomer molecules move passively by the kinetic energy of other molecules whereas in microwave polymerization, the monomer molecules move with the internal heat that is produced via high frequency electromagnetic field; in other words, heat generation is the consequence of movement of molecules.¹³ In the microwave case, heat transfer is achieved via radiative heat transfer whereas in the conventional heat polymerization method heat is transferred via conduction. The activity of monomers increases via the microwave energy transferred; thus, the polymerization rate increases while the residual monomer content in the polymeric matrix decreases.

Regarding the oxygen inhibition, it was observed that the oxygen inhibition layer was thicker in the samples with the glass fiber weave than in those without the glass fiber weave due to the some voids left within the matrix that acts as oxygen reserves and allows oxygen to inhibit polymerization.¹⁶ In parallel, oxygen inhibition of the polymerization process gives a plausible explanation for this study. This inhibition was expected to be more dominant for the case of the conventional heat-polymerized resin compared to the microwave-polymerized resin due to the longer polymerization period. The reason for the highest residual monomer content of woven e-glass fiber reinforcement with conventional heat-polymerized denture base could be probably due to the improper binding of resin with fiber, incorporation of oxygen into the polymeric matrix, and relatively higher oxygen inhibition than other fiber types.

A number of methods have been developed to determine the level of residual monomer content in acrylic resins.¹⁷ HPLC method is suitable for the analysis of several organic and inorganic compounds including polar and ionic molecules; moreover, the method allows using several sensitive detector systems, in addition it provides accurate estimation of the level of residual monomer in acrylic resins. Besides, in this technique all procedures are carried out in the liquid at room temperature, thus this method enhances precise results.^{8,18}

Glass and polyethylene fibers have increased usage and application recently, and in this study HPLC technique was used to determine the effects of fiber reinforcement on the residual monomer content of heat-polymerized and microwave-polymerized denture base materials. Although there were several studies carried out to detect the residual monomer content of acrylic resins via HPLC technique,^{8,17–20} very limited studies were carried on the effect of fiber reinforcement on the residual monomer content determined via HPLC method. Bayraktar et al.,¹⁰ studied the residual monomer content of unreinforced and e-glass fiber reinforced test specimens by HPLC technique. In the present study, not only glass fiber but also polyethylene fiber was used as reinforcing agent.

Studies by Kalıpçılar et al.,²¹ Vallittu,²² Doğan et al.,⁷ and Bartoloni et al.⁵ showed that polymerization methods, polymerization temperature, and polymerization time affect the residual monomer content of denture base resins. Bayraktar et al.¹⁰ evaluated the residual monomer content of unreinforced and e-glass fiber-reinforced (11.5% per weight) test specimens, polymerized with heat and microwave energy by HPLC, and results has shown significant differences between unreinforced and fiber-reinforced samples. A larger amount of residual monomer content was released from the heat-polymerized test specimens than from the microwave-polymerized test specimens. Moreover, Bayraktar et al.¹⁰ stated that “generally residual MMA was found more in glass fiber reinforced test groups than unreinforced groups,” these results were parallel to the findings in the current study.

Conventional heat-polymerized denture base resins reinforced with fiber systems has higher water absorption than that of microwave heat-polymerized denture base resins reinforced with fiber systems except for one fiber type²³; in parallel, a similar statement could be concluded for the residual monomer content of denture base resin. In other words, conventional heat-polymerized denture base resins reinforced with fiber system has higher residual monomer content than that of microwave-polymerized denture base resin reinforced with fiber. There could be a direct or indirect correlation between water absorption and residual monomer content for the denture base materials, that is, water absorption might increase in the polymeric matrix that contains relatively high residual monomer, and a proper network formation was not achieved within the matrix. Water diffusion would be more difficult in case where a good polymer network is formed and in which the residual monomer content is relatively low. A parallel result was obtained and stated that the level of residual monomer determined by gas-liquid chromatography decreases with the increase

in curing time and temperature while the tensile strength was improved and water absorption decreased.⁷

In the previous study, it was observed that the microwave-polymerized denture base material reinforced with fiber have higher transverse strength and elastic modulus values than the heat-polymerized denture base materials reinforced with continuous parallel e-glass fiber, woven e-glass fiber, and woven polyethylene fiber.¹² The results in this study for the residual monomer content was the just reverse, that is, microwave-polymerized denture base material reinforced with continuous parallel e-glass fiber, woven e-glass fiber, and woven polyethylene fiber have lower residual monomer content than the heat-polymerized denture base materials reinforced with continuous parallel e-glass fiber, woven e-glass fiber, and woven polyethylene fiber. Theoretically, polymer including nonpolymerized monomer units would have lower mechanical properties compared with polymer without any monomer units for the same defined basis. It could be stated that the higher the residual monomer content, the lower the mechanical properties of the polymer matrix. However, since fiber reinforcement might increase the residual monomer content that might diffuse from acrylic resin resulting in adverse effects such as redness, swelling, and pain on the oral mucosa,^{5,9,10} the use of fiber reinforcement should be carefully considered during the preparation of denture base material.

CONCLUSIONS

Conventional heat polymerization resulted in a higher residual monomer content compared with microwave polymerization for fiber-reinforced denture base resin, probably due to the oxygen inhibition. Continuous parallel e-glass fiber, woven e-glass fiber, and polyethylene fiber in woven form reinforcements increased the residual monomer content significantly for conventional heat-polymerized case, and this effect was statistically insignificant for microwave-polymerized case. Woven e-glass fiber reinforcement with conventional heat-polymerized denture base resin showed the highest residual monomer content. Polyethylene fiber in woven form has lower residual monomer content compared with e-glass fiber for conventional heat-polymerized resin case.

References

1. Phoenix, R. D. *Dent Clin North Am* 1996, 40, 113.
2. Craig, R. G.; Hanks, C. T. *Restorative Dental Materials*; Mosby: St. Louis, 1993.
3. Usanmaz, A.; Ateş, J.; Doğan, A. *J Appl Polym Sci* 2003, 90, 251.

4. Vallittu, P. K.; Miettinen, V.; Alakujala, P. *Dent Mater* 1995, 11, 338.
5. Bartoloni, J. A.; Murchison, D. F.; Wofford, D. T.; Sarkar, N. K. *J Oral Rehabil* 2000, 27, 488.
6. Vallittu, P. K.; Ruyter, I. E.; Buyukyilmaz, S. *Eur J Oral Sci* 1998, 106, 588.
7. Doğan, A.; Bek, B.; Cevik, N. N.; Usanmaz, A. *J Dent* 1995, 23, 313.
8. Urban, V. M.; Cass, Q. B.; Oliveira, R. V.; Giampaolo, E. T.; Machado, A. L. *Biomed Chromatogr* 2006, 20, 369.
9. Yılmaz, H.; Aydın, C.; Çağlar, A.; Yaşar, A. *Quintessence Int* 2003, 34, 148.
10. Bayraktar, G.; Duran, O.; Guvener, B. *J Dent* 2003, 31, 297.
11. Cokeliler, D.; Erkut, S.; Zemek, J.; Biederman, H.; Mutlu, M. *Dent Mater* 2007, 23, 335.
12. Köroglu, A.; Özdemir, T.; Usanmaz, A. *J Appl Polym Sci* 2009, 113, 716.
13. Çelebi, N.; Yüzügüllü, B.; Canay, Ş.; Yücel, Ü. *Polym Adv Technol* 2008, 19, 201.
14. Memon, M. S.; Yunus, N.; Razak, A. A. A. *Int J Prosthodont* 2001, 14, 214.
15. Rizzatti-Barbosa, C. M.; Del Bel Cury, A. A.; Garcia, R. The Use of Microwave Energy in Dental Prosthesis, In: *Advances in Induction and Microwave Heating of Mineral and Organic Materials*; Stanislaw, G., Ed.; I-Tech Education and Publishing: Austria, 2011.
16. Vallittu, P. K. *J Mater Sci Mater Med* 1997, 8, 489.
17. Shim, J. S.; Watts, D. C. *Dent Mater* 1999, 15, 296.
18. Urban, V. M.; Machado, A. L.; Oliveria, R. V.; Vergani, C. E.; Pavarina, A. C.; Cass, Q. B. *Dent Mater* 2007, 23, 363.
19. Lee, S. Y.; Lai, Y. L.; Hsu, T. S. *Eur J Oral Sci* 2002, 110, 179.
20. Snauko, M.; Berek, D.; Hunkeler, D. *J Chromatogr A* 2005, 1084, 173.
21. Kalıpçılar, B.; Karağaçoğlu, L.; Hasanreisioğlu, U. *J Oral Rehabil* 1991, 18, 399.
22. Vallittu, P. K. *J Oral Rehabil* 1995, 22, 257.
23. Durkan, R. K.; Özdemir, T.; Pamir, A. D.; Usanmaz, A. *J Appl Polym Sci* 2010, 117, 1750.