

EFFECT OF CURING REGIMES ON PHYSICAL PROPERTIES OF HEAT CURE ACRYLIC RESIN

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ABSTRACT

This study was conducted to determine the effect of varying curing conditions on the residual monomer concentrations of heat cure acrylic denture resin.

Sixty-four disc shaped acrylic resin specimens were processed at four powder-liquid ratios (2.22, 2.00, 1.80 and student-ratio) and cured in a heated water bath using 4 different curing regimes (two with a terminal boil and two without). The residual monomer concentrations were determined at intervals of 24, 48 and 72 hours using a UV Spectrophotometer.

The results indicated a decrease in residual monomer concentration with storage time. Group 4 (student-ratio) and curing by cycle 2B (placing the assembly in the water bath directly at 100°C) showed the highest overall residual monomer concentrations while group 1 (highest powder-liquid ratio) and curing by cycle 1A showed the least overall residual monomer concentrations

It was concluded that students dispensing acrylic powder and liquid monomer without calculations would lead to higher residual monomers if a proper curing regime is not followed. Using a 60 minute terminal boil in the polymerization process is strongly recommended. Storing the acrylic denture bases for at least 24-48 hours in water before use will decrease residual monomers being leached into the oral environment.

INTRODUCTION

In spite of the extensive use of Polymethyl-methacrylate (PMMA) in dentistry, complications associated with their inherent property related limitations and processing have been documented.¹ One of the problems associated with acrylic dentures is the presence of residual monomers following fabrication.² Studies have shown that polymerization of methylmethacrylate is never quite complete and despite long curing cycles of polymerization minimal amounts of un-polymerized residual monomer can always be found.³ Mechanical and biological consequences of un-polymerized residual monomers have also been studied extensively.^{4,5} A number of studies have reported various degrees of in-vitro cytotoxicity and in-vivo allergic responses to

leached residual monomers.⁶⁻⁹ Mechanical properties of acrylic denture base resins, such as hardness and flexural strength, have also been known to be adversely affected by the extent of un-polymerized monomers within the matrix.^{10,11}

In the past few years, various processing methods and material variations have been introduced to improve the mechanical, physical and biological properties of cured acrylic resins.¹²⁻¹⁶ Researchers have introduced a number of curing techniques to achieve a maximum monomer to polymer conversion to produce acrylic with superior properties.¹⁷ Methods such as the introduction of microwaves and visible light activated curing techniques to reduce the curing time, have revolutionized the science of denture acrylics. However, curing acrylic dentures in the conventional water bath still remains the most widely used method.¹⁸

According to the ISO 20795-1:2008 standard, the maximum acceptable quantity of residual monomers in acrylic should not be more than 2.2% by weight.^{19,20} However, clinical reports have shown the presence of variable amounts of residual monomers in an acrylic dentures base.^{7,21-23} Factors such as temperature, time, initiator concentration, curing environment (water bath v/s microwave), pressure, mixing ratio and denture base thickness have an effect on the residual monomer content.^{23,24} One additional factor affecting the cytotoxicity of acrylic is the polymer powder to monomer liquid ratio.^{25,26}

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The amount of residual monomer in an acrylic resin denture base, has been determined using various methods. Fourier Transformation Infrared (FTIR), Ultraviolet and Visible Spectrophotometry, High Pressure Liquid Chromatography and Gas Chromatography (GC) have been most popular.²⁶⁻²⁹ The aim of this study is to determine and compare the effects of varying powder liquid ratios and curing cycles on the residual monomer concentration of cured acrylic resins. Residual monomer concentrations would be determined for acrylic specimens made at the manufactures recommended powder-liquid ratio as well as those dispensed by under-graduate dentistry students.

METHODOLOGY

a) Preparation of a standard mould

Poly-tetra-fluoroethylene (Teflon) rods having a diameter of 38.1mm (1.5 inches) were cut into 12 discs each having a thickness of 25.4mm. These Teflon discs were subjected to a milling process in order to create a 4mm deep hollow cavity with a precise diameter of 32mm. The created cavities would serve as moulds for the fabrication of the heat cured acrylic discs.

b) Preparation of acrylic specimens

The heat cure acrylic powder was mixed with methyl-methacrylate liquid monomer according to ratios mentioned in Table 1. The heat cure liquid was placed into a clean dry mixing vessel and the powder was sprinkled onto the liquid over a period of 30 seconds according to manufacturer recommendations.³⁰ A spatula was used to mix the material which was finally packed at the doughy stage into the moulds and each covered with a polyethylene sheet. The dental flasks were placed in a hydraulic bench press (Dental Hydraulic Flask Press, BISON, Intensiv Industries, India) under a pressure of 8000 kPa for 25 mins.³⁰ The flasks were then immersed in water and cured using an electrically controlled water bath according to the regimes mentioned in Table 2.

The four groups (G1-G4) are based on varying powder liquid ratios, with each group having to undergo four curing cycles (1A, 1B, 2A and 2B). Sixteen specimens of acrylic discs were created for each group translating to a total of 64 discs. Group G4 constituted specimens processed at un-calculated powder-liquid ratios dispensed by 16 final year BDS students at the Islamic International Dental College, Islamabad, Pakistan. The amount of monomer leached from each specimen was measured at an interval of 24 hours, 48 hours and 72 hours in the UV spectrophotometer.

c) Curing cycles for the test specimens

- Cycle 1A: The flasks were immersed in a water bath at room temperature (25°C). The temperature was then gradually increased to 70°C (165°F) and maintained for 90 minutes. The temperature was then raised to 100°C (212°F) and maintained for 60 minutes.

- Cycle 1B: The flasks were immersed in a water bath at room temperature. The temperature was gradually increased to 70°C and maintained for 60 minutes. The temperature was then raised to 100°C and maintained for 30 minutes.
- Cycle 2A: The flasks were immersed in a water bath having a temperature of 70°C and the temperature was gradually increased to 100°C and maintained for 30 minutes.
- Cycle 2B: The flasks were immersed in a water bath having a temperature of 100°C and cured for 30 mins.

Following the completion of the mentioned curing cycles, the flasks were allowed to cool to room temperature. The acrylic specimens were removed and finished using an acrylic trimmer and sandpaper. Polishing of the specimens was done with pumice slurry on a lathe polishing buff.

d) Formation of a standard calibration curve

A stock solution of 3%v/v methylmethacrylate was initially prepared by dissolving 3ml of methylmethacrylate in 100ml of distilled water. From this stock solution, a series of aliquots ranging from 0.5% to 3.0% were created by simply diluting the stock with specific volumes of distilled water. Absorbance of these solutions was determined at 210nm using the UV spectrophotometer to obtain a standard graph of concentration against absorbance (Fig 1). The standard calibration curve is then used to determine the amount of methylmethacrylate leached from the 64 acrylic discs.

e) Residual monomer determination of acrylic specimens:

Each of the 64 acrylic specimens was immersed in 15ml of distilled water and subjected to UV spectroscopy at 210nm after intervals of 24, 48 and 72 hours. The amount of residual monomer leached into the distilled water was analyzed and values compared with the standard graph.

RESULTS

The mean of the residual monomer measurements for the 4 groups are represented in Fig 2. A linear regression analysis was carried out showing values of residual monomer concentration and variables of powder-liquid ratios, curing cycles and storage time are statistically significant with a p-value of 0.000. Moderately strong negative correlation (-0.515) exists between time and residual monomer concentration, indicating residual monomers decrease with storage

TABLE 1: POWDER LIQUID RATIOS

	Powder	Liquid
G1	23.4gm	9ml
G2	23.4gm	10ml
G3	23.4gm	11ml
G4	Students ratio	

TABLE 2: CURING CYCLES OF THE RESINS T0: START TEMPERATURE OF WATER, T1 AND T2: TEMPERATURE OF WATER DURING POLYMERIZATION CYCLE T0, T1, T2: MAINTAINING TIME AT THE RELATIVE TEMPERATURES

	T0	t0	T1	t1	T2	t2
1A	25°C	0 min	70°C	90 min	100°C	60 min
1B	25°C	0 min	70°C	60 min	100°C	30 min
2A	70°C	0 min	100°C	30 min	—	—
2B	100°C	0 min	100°C	30 min	—	—

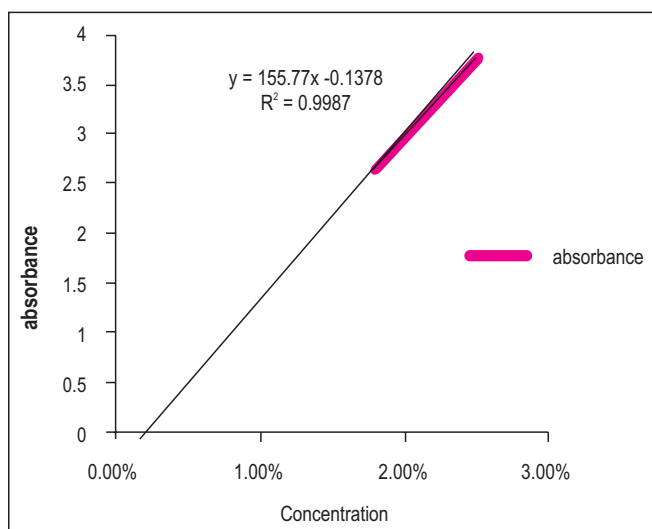


Fig 1: Standard Calibration Curve

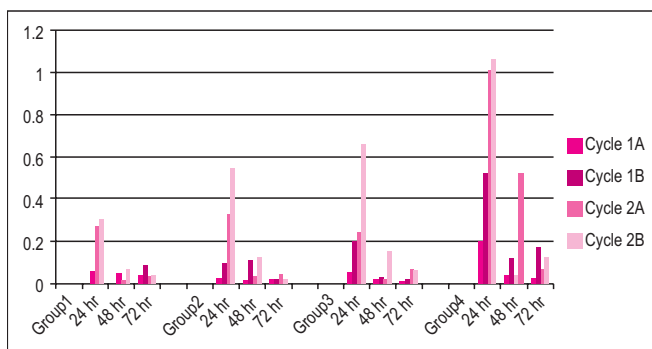


Fig 2: Graphical representation of mean residual monomer concentration of the four groups.

time. Group 4 (student-ratio) and Cycle 2B (insertion of the curing assembly in the water bath at 100°C) showed the highest overall residual monomer concentrations, while Group 1 (highest powder-liquid ratio) and Cycle 1A (immersing the flask in water bath at room temperature, gradually increasing the temperature to 70°C and maintaining it for 90 minutes, followed by increasing the temperature to 100°C and maintaining it for 60 minutes) showed the least overall residual monomer concentration.

Independent sample t tests were used to compare the residual monomer concentration of samples cured using Cycle 1A to those cured with Cycle 2B, as well as

Cycles 1A and 1B. The mean residual monomer concentration of samples cured by Cycle 2B (0.27 ± 0.313) was found to be greater than the mean residual monomer concentration (0.04 ± 0.05) of samples cured by Cycle 1A (p value = 0.00). Based on these results it may be suggested that Cycle 1A will produce less residual monomers, irrespective of the powder liquid ratio, compared to Cycle 2B. Hence the powder liquid ratio used by the students (Group 4) would not influence the residual monomer concentration if an appropriate curing cycle (such as Cycle 1A) is adhered to.

The mean residual monomer concentration of samples cured by Cycle 1A (0.04 ± 0.05) was found to be less than the mean residual monomer concentration (0.125 ± 0.132) of samples cured by Cycle 1B (p value 0.00). These results suggest that decreasing the curing time and the terminal boil period by 30 minutes produces more residual monomers.

DISCUSSION

In this study UV spectrophotometer was used to determine the amount of monomer released into distilled water.^{21,31} The results suggest that curing cycles have a higher positive correlation (0.361) as compared to powder-liquid ratio (0.30), which is in agreement with Jerolimov et al³², who stated that the choice of curing cycle has much greater influence on the level of residual monomer as compared to the mixing ratio.

Group 4 of our study constituted samples prepared by 4th year undergraduate students dispensing and mixing the acrylic powder and liquid under supervision (to ensure that they follow the standard mixing techniques recommended by the manufacturer). It was noted that the students mixed the acrylic resin normally without following any ratio or measuring system. A powder-liquid ratio of 2.34:1 is recommended by the manufacturer, which limits the volumetric contraction during polymerization as well as excess un-polymerized monomer.² When an acrylic denture is prepared with a higher proportion of polymer at a higher powder-liquid ratio, the levels of residual monomer appears to be low.³³ As shown in Fig 2, decreasing the powder-liquid ratio from group 1 to group 3, caused an increase in residual monomer concentrations. The lowest values of residual monomer were found in Group 1 where the powder-liquid ratio was highest. The highest residual monomer concentration was seen in the student group

which indicated students seem to dispense more liquid monomer resulting in a lower powder-liquid ratio.

As the use acrylic resins has dramatically increased, different curing cycle have been introduced with the express purpose of achieving a higher monomer to polymer conversion. Variations in curing temperatures and soak times have been documented. However, in this study 4 short cycles were selected based on the cycles commonly used by students and laboratory technicians.^{34,35}

In Cycle 1A and 1B the flasks were kept in a water bath at room temperature and the temperature was gradually increased. The rate at which the material reaches its maximal temperature has to be carefully controlled in order to avoid gaseous porosity.³⁴ It seems from our results that gradually increasing the temperature and curing time lead to a decrease in the residual monomer content, whereas, placing the flasks directly at high temperatures caused an increase in residual monomer content which is also in agreement with other studies.³⁶

Although the powder-liquid ratio used in group 2 was recommended by manufacturer, and the residual monomer content in group 2 increased from cycle 1A (0%) to cycle 2B (0.305%) in 24 hours. These results indicate that short curing cycles and curing acrylic resins at increased temperatures release more residual monomers. The initiator, benzoyl peroxide decomposes above 60°C, giving free radicals which start and propagate polymerization.³⁷ The decomposition of benzoyl peroxide is temperature dependent, hence in long curing cycle greater decomposition of benzoyl peroxide results in greater number of polymer chains. Conversion of monomer to polymer is time dependent and the rate of conversion is greatly increased by increasing the temp from 70°C to 100°C.³⁴

According to Harrison and Huget, the most effective polymerization cycle with minimal levels of residual monomer was a 7 hour incubation in water at 70°C followed by a post polymerization treatment at 1 hour at 100°C.³⁸ Although many authors prefer long curing cycles, Bayraktar et al³⁹ found that long curing cycles (9 hours at 70°C) without post polymerization terminal boil showed higher content of residual monomer as compared to a shorter cycle followed by a short terminal boil (20 minutes at 70°C, followed by 22 minutes at 100°C). Hence to reduce the final residual monomer content, a final post polymerization treatment (terminal boil, microwaving for few minutes or immersing in water for at least 24 hours) is most effective.^{7,39-41} Cycles 1A and 1B underwent a terminal boil post polymerization treatment, which could be the reason for low residual monomer content.

As the polymerization reaction proceeds, the amount of monomer and free radicals decrease and due to increase in viscosity and degree of polymerization, it becomes difficult to bring the monomer and free radical together. Hence the diffusion of monomer becomes the rate-limiting step. Increasing the temperature causes

the molecules to move faster and the polymerization reaction will be more complete.²¹

The release of MMA into water decreases with time. In this study maximum release of residual monomer occurs in the first 24 hours. The decrease of release of MMA in water could be due to hydrolysis of methylmethacrylate to methacrylic acid and methanol as well as due to continued polymerization of the resin⁴², hence storing the acrylic resin denture for at least 24-48 hours before insertion is recommended.

The highest amount of residual monomer content was leached from Group 4. It seems that our under-graduate students dispense more liquid monomer than required. If such a mix is to produce a processed denture base with minimal amounts of residual monomers, a water bath curing regime involving a gradual increase in temperature and curing time followed by a terminal boil for 60 minutes should be adopted. Ideally students should follow powder-liquid ratios recommended by manufacturers and hence adequate gauging facilities should be made available at dental colleges.

CONCLUSION

- 1 Curing regimes influence residual monomer concentration more as compared to the powder liquid ratio.
- 2 Specimens cured using curing cycles starting at room temperature, followed by gradually increasing the temperature seem to exhibit lower values of residual monomers at compared to placing the flasks directly into boiling water.
- 3 The release of residual monomer decreases with storage time.

REFERENCES

- 1 Bhola R, Bhola SM, Liang H, Mishra B. Biocompatible Denture Polymers-a review. Trends in Biomaterials and Artificial Organ. 2010; 23(3): 129-36.
- 2 Anusavice KJ, Phillips RW, Shen C, Rawls HR. Phillips' science of dental materials: Elsevier Health Sciences; 12th Edition. 2012.
- 3 FM Huang CH, YC Chang, MY Chou. Residual monomer releasing from acrylic resin denture base in water. Chinese Dental Journal. 2000; 19(1): 17-22.
- 4 Bettencourt AF, Neves CB, de Almeida MS, Pinheiro LM, Lopes LP, Castro MF. Biodegradation of acrylic based resins: A review. Dental Materials. 2010; 26(5): 171-80.
- 5 Ivković N, Božović D, Ristić S, Mirjanić V, Janković O. The residual monomer in dental acrylic resin and its adverse effects. Contemporary Materials. 2013; 1(4): 84-91.
- 6 Bural C, Aktas E, Deniz G, Unlucerci Y, Kızılcan N, Bayraktar G. Effect of post-polymerization heat-treatments on degree of conversion, leaching residual MMA and in vitro cytotoxicity of autopolymerizing acrylic repair resin. Dental Materials. 2011; 27(11): 1135-43.
- 7 Bural C, Aktas E, Deniz G, Unlucerci Y, Bayraktar G. Effect of leaching residual methyl methacrylate concentrations on in vitro cytotoxicity of heat polymerized denture base acrylic resin processed with different polymerization cycles. Journal of Applied Oral Science. 2011; 19(4): 306-12.
- 8 de Andrade Lima Chaves C, Machado AL, Vergani CE, de Souza RF, Giampaolo ET. Cytotoxicity of denture base and hard chairside relined materials: a systematic review. The Journal of Prosthetic Dentistry. 2012; 107(2): 114-27.

- 9 Martin N, Bell HK, Longman LP, King CM. Orofacial reaction to methacrylates in dental materials: a clinical report. *The Journal of Prosthetic Dentistry*. 2003; 90(3): 225-27.
- 10 Mese A, Guzel KG. Effect of storage duration on the hardness and tensile bond strength of silicone-and acrylic resin-based resilient denture liners to a processed denture base acrylic resin. *The Journal of Prosthetic Dentistry*. 2008; 99(2): 153-59.
- 11 Sato T, Takahashi H, Hongo T, Hayakawa I. Effect of degradation of denture base resin on bond strength to relining resins. *Dental Materials Journal*. 2007; 26(1): 89-95.
- 12 Murakami N, Wakabayashi N, Matsushima R, Kishida A, Igarashi Y. Effect of high-pressure polymerization on mechanical properties of PMMA denture base resin. *Journal of the mechanical behavior of biomedical materials*. 2013; 20: 98-104.
- 13 Negrutiu M, Sinescu C, Romanu M, Pop D, Lakatos S. Thermoplastic resins for flexible framework removable partial dentures. *Tinisora Medical Journal*. 2005; 55(3): 295-99.
- 14 Elshereksi N, Malaysia US. Effect of filler incorporation on the fracture toughness properties of denture base poly (methyl methacrylate). *Journal of Physical Science*. 2009; 2(2): 1-12.
- 15 Ali IL, Yunus N, Abu-Hassan MI. Hardness, flexural strength, and flexural modulus comparisons of three differently cured denture base systems. *Journal of Prosthodontics*. 2008; 17(7): 545-49.
- 16 Celebi N, Yuzugullu B, Canay S, Yucel U. Effect of polymerization methods on the residual monomer level of acrylic resin denture base polymers. *Polymers for Advanced Technologies*. 2008; 19(3): 201-6.
- 17 Sedda M, Borracchini A, Monticelli F, Goracci C, Ferrari M. Influence of the polymerization cycle on the flexural strength of four different PMMA-based heat-polymerized denture base resins. *International Dentistry South Africa*. 2006; 8(3): 20-24.
- 18 Ghani F, Kikuchi M, Lynch C, Watanabe M. Effect of some curing methods on acrylic maxillary denture base fit. *The European Journal of Prosthodontics and Restorative Dentistry*. 2010; 18(3): 132-38.
- 19 Standard I. ISO 1567 for Dentistry-Denture base polymers. 1999.
- 20 International Organization for Standardization. Dentistry — Base polymers — Part 1: Denture base polymers. 2008; ISO 20795-1: 2008(E).
- 21 Rao S, Mahesh P. Comparison of residual monomer and water absorption in acrylic resin samples processed with microwave and conventional heat cure polymerization methods-in vitro study. *Annals and Essence of Dentistry Journal*. 2012; 4(1): 25-29.
- 22 Lung C, Darvell B. Minimization of the inevitable residual monomer in denture base acrylic. *Dental Materials*. 2005; 21(12): 1119-28.
- 23 Pfeiffer P, Rosenbauer E-U. Residual methyl methacrylate monomer, water sorption, and water solubility of hypoallergenic denture base materials. *The Journal of Prosthetic Dentistry*. 2004; 92(1): 72-8.
- 24 Azzarri M, Cortizo M, Alessandrini J. Effect of the curing conditions on the properties of an acrylic denture base resin microwave-polymerised. *Journal of Dentistry*. 2003; 31(7): 463-68.
- 25 Lamb D, Ellis B, Priestley D. The effects of process variables on levels of residual monomer in autopolymerizing dental acrylic resin. *Journal of Dentistry*. 1983; 11(1): 80-88.
- 26 Kedjarune U, Charoenworakul N, Koontongkaew S. Release of methyl methacrylate from heat-cured and autopolymerized resins: Cytotoxicity testing related to residual monomer. *Australian Dental Journal*. 1999; 44(1): 25-30.
- 27 Imazato S, McCabe J, Tarumi H, Ehara A, Ebisu S. Degree of conversion of composites measured by DTA and FTIR. *Dental Materials*. 2001; 17(2): 178-83.
- 28 Duray SJ, Gilbert JL, Lautenschlager EP. Comparison of chemical analysis of residual monomer in a chemical-cured dental acrylic material to an FTIR method. *Dental Materials*. 1997; 13(4): 240-45.
- 29 Sadamori S, Kotani H, Hamada T. The usage period of dentures and their residual monomer contents. *The Journal of Prosthetic Dentistry*. 1992; 68(2): 374-76.
- 30 Dental M. Meadway Supercure [cited 2015 28-02-2015]. Available from: <http://www.mrdental.co.uk/Heat-Cure-Denture-Base/Meadway-Supercure.html?cPath=2>.
- 31 Oliveira V, Leon B, Del Bel Cury A, Consani S. Influence of number and position of flasks in the monomer release, Knoop hardness and porosity of a microwave-cured acrylic resin. *Journal of Oral Rehabilitation*. 2003; 30(11): 1104-8.
- 32 Jerolimov V, Huggett R, Brooks S, Bates J. The effect of variations in the polymer/monomer mixing ratios on residual monomer levels and flexural properties of denture base materials. *Quintessence of Dental Technology*. 1985; 9(7): 431.
- 33 Jorge JH, Giampaolo ET, Machado AL, Vergani CE. Cytotoxicity of denture base acrylic resins: a literature review. *The Journal of Prosthetic Dentistry*. 2003; 90(2): 190-93.
- 34 Ghani F, Moosa R. Effect of curing methods and temperature on porosity in acrylic resin denture bases. *Journal of Pakistan Dental Association*. 2012; 21(03).
- 35 Lopes MC, Consani RLX, Mesquita MF, Sinhoreti MAC, Consani S. Effect of monomer content in the monomer-polymer ratio on complete denture teeth displacement. *Brazilian Dental Journal*. 2011; 22(3): 238-44.
- 36 Vallittu PK, Ruyter I, Buykilmaz S. Effect of polymerization temperature and time on the residual monomer content of denture base polymers. *European Journal of Oral Sciences*. 1998; 106(1): 588-93.
- 37 Vallittu PK, Miettinen V, Alakuijala P. Residual monomer content and its release into water from denture base materials. *Dental Materials*. 1995; 11(5): 338-42.
- 38 Harrison A, Huggett R. Effect of the curing cycle on residual monomer levels of acrylic resin denture base polymers. *Journal of Dentistry*. 1992; 20(6): 370-74.
- 39 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. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2006; 76(2): 340-45.
- 40 Urban VM, Machado AL, Oliveira RV, Vergani CE, Pavarina AC, Cass QB. Residual monomer of relined acrylic resins: Effect of water-bath and microwave post-polymerization treatments. *Dental Materials*. 2007; 23(3): 363-68.
- 41 Gautam R, Singh RD, Sharma VP, Siddhartha R, Chand P, Kumar R. Biocompatibility of polymethylmethacrylate resins used in dentistry. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2012; 100(5): 1444-50.
- 42 Honorez P, Catalan A, Angnes U, Grimonster J. The effect of three processing cycles on some physical and chemical properties of a heat-cured acrylic resin. *The Journal of Prosthetic Dentistry*. 1989; 61(4): 510-7.

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| 2 Faisal Moeen: | Conceived and designed the study and wrote the article. |
| 3 Yawar Hayat Khan: | Planned the research and reviewed the article. |