An in vitro study to evaluate and compare the effects of various polymerisation cycles on the physical and mechanical properties of Heat cure Polymethylmethacrylate resin.

Dr Suvidha S. Patil[1], Dr Anandkumar G. Patil[2], Dr Hema Kanathila[3], Dr Sounyala R[4]

[1]Lecturer, Department ofProsthodonticsand crown and bridge, KAHER'SKLE V. K. Institute of Dental Sciences, Nehru Nagar, Belgaum, Karnataka, India

[2]Professor and Head, Department ofProsthodonticsand crown and bridge, KAHER'S KLE V. K. Institute of Dental Sciences, Nehru Nagar, Belgaum, Karnataka, India

[3]Professor, Department ofProsthodonticsand crown and bridge, KAHER'SKLE V. K. Institute of Dental Sciences, Nehru Nagar, Belgaum, Karnataka, India

[4]Professor, Department ofProsthodonticsand crown and bridge, KAHER'SKLE V. K. Institute of Dental Sciences, Nehru Nagar, Belgaum, Karnataka, India

ABSTRACT

Background: The most widely used resin for denture bases is heat-cure acrylic (HCA). The curing cycle (CC) utilised has an impact on the material's physical and mechanical properties. Identification of an ideal CC is required to achieve maximum monomer-to-polymer conversion and chain branching/cross-linking.

Objective: To evaluate and compare the effects of different CC on residual monomer content, porosity and flexural strength of denture base resins.

Methods: Two-hundred standard-sized HCA samples were processed using 4 different CC (50 samples per CC) - Group I (9 hours at 74°C); Group II (2 hours at 74°C and 1 hour at 100°C); Group III (1 hour at 74°C and 30 minutes at 100°C); and Group IV (30 minutes at 74°C and 15 minutes at 100°C).Following that, samples were tested for their residual monomer content, porosity and flexural strength using UV spectrophotometer, stereomicroscope and universal testing machine, respectively. The

data was statistically analyzed using ANOVA and Tukey's post-hoc test. p-value ≤ 0.05 indicated statistical significance.

Results: Group I had the highest mean flexural strength (120.07 ± 6.99 MPa), followed by Group II, Group III, and Group IV. The mean residual monomer content and porosity values were lowest in Group I (0.19 ± 0.03 and 12.28 ± 4.16, respectively), followed by Group II, Group III, and Group IV, with statistically significant differences ($p<0.05$) across the groups.

Conclusion: In comparison to short curing cycles with bench curing, long curing cycle (9 hours at 74°C) is associated with higher flexural strength and lower residual monomer content and porosity.

KEYWORDS: Polymethyl methacrylate, Dentures, Flexural strength, Porosity, Polymerization

INTRODUCTION

Since the 19th century, several polymers, including vulcanised rubber, polystyrene, polyvinyl acrylic, and polymethyl methacrylate (PMMA), have been utilised to make denture base resins (DBR), with PMMA remaining the most commonly used material due to its superior qualities. [1] It is frequently used to make maxillofacial prostheses, interim prostheses, removable complete and partial dentures, and fixed partial prostheses. [1,2]Due to its many benefits, like good dimensional stability and transverse strength, less residual monomer and porosities, greater ease of processing and handling, and the ability to mould into complex forms with the application of pressure and heat, heat-cure (HC) PMMA is more widely used than auto-polymerizing resin (APR). [2] It aids in overcoming some of APR's shortcomings, including higher levels of

residual monomer following complete polymerization, which causes more polymerization shrinkage, porosities, and poorer mechanical and physical properties.[2]

The method used to produce the polymer-monomer mixture has an impact on how PMMA polymerizes, and it cures by an addition polymerization reaction. [3] The initiator, benzoyl peroxide, must be activated above 60 degrees Celsius in order to release free radicals (FR), which propagates polymerization by opening the double bonds in MMA and starting a chain reaction. [3] By raising the temperature from 70°C to 100°C, the rate of this reaction is significantly increased.[4] Long or short conventional curing cycles may be followed by terminal boiling. [4]Commercial laboratories find it difficult to use since the long cycle cannot entirely transform monomer into polymer, leading to worse mechanical properties and time commitments. [4] The entire conversion of monomer to polymer during a long cycle results in better mechanical qualities, but the lack of terminal boiling causes more residual monomer and increases the time requirements, making it challenging to utilise in commercial laboratories. With the short cycle, these limitations have been removed.[4]

Identification of the ideal curing regime is justified by the requirement for maximum monomer-to-polymer conversion, chain branching, and cross-linking in order to produce a higher molecular weight polymer with improved mechanical properties. While various studies have independently assessed various mechanical factors, it is necessary to examine these parameters in a single study. This invitrostudy assesses and compares how different curing cycles affect the porosity, flexural strength, and residual monomer content of heat cure denture base resins.

MATERIALS AND METHODS

This in vitro study was conducted in KAHER s KLE VK Institute of Dental Sciences, Belgaum, Karnataka, India, after obtaining ethical clearance from the Institutional Review Board. Two hundred HC PMMA acrylic resin samples of standard size (64 mm length, 10 mm breadth, and 3 mm width) were fabricated using standard master dies (Figure-1A) and processed using 4 different curing cycles (50 samples per curing cycle), followed by sample evaluation.

Acrylic sample fabrication: Metal die moulds were prepared for this, by investing the dies in one half of a metal flask with type III gypsum product (Kalabhai, Kalstone) and covering them with additional silicone putty and elastomeric material (3M ESPE soft putty).After the material was set in the remaining half of the flask, silicone putty was adapted on the open surface of the invested metal die models to form a lid. The remaining half of the flask was placed in position to ensure complete closure, and investing was completed using the two-pour technique. A heat-cure acrylic denture base material with an accepted polymer to monomer ratio of 3:1 by volume was prepared. The resin was packed into premade moulds as soon as the mass reached the dough stage and did not stick to the mixing vessel or spatula surfaces. During the trial packing, a closing pressure of roughly 200 psi was gently applied with a hydraulic press to allow the extra flash to flow out between the two ends of the flask, and this excess was eliminated.The flasks were then bench cured for 60 minutes for the purpose of equalizing pressure in the mould, release internal stresses and allow dispersion of monomer uniformly.Following this, flasks were submerged in an acrylizer (Confident Acrylizer C-73A) that contained water at room temperature. The temperature in the

acrylizer was then adjusted to the desired level for curing the samples in accordance with the curing cycle followed.

Curing and processing -Based on the length of the curing cycles, the samples were divided into four groups: Group I (50 samples processed for 9 hours at 74°C); Group II (50 samples processed for 2 hours at 74°C and 1 hour at 100°C); Group III (50 samples processed for 1 hour at 74°C and 30 minutes at 100°C); and Group IV (50 samples processed for 30 minutes at 74°C and 15 minutes at 100°C). After curing, the flasks were given 30 minutes to bench cool at room temperature and an additional 30 minutes to cool under running water. Using tungsten carbide burs, the samples were deflashed, recovered, and grossly finished (Figures-1B and 1C).

Acrylic sample evaluation -Twenty-five samples from each group were then evaluated for their residual monomer content, while the remaining 25 samples were evaluated for porosity and flexural strength, using ultraviolet (UV) spectrophotometer (Sshimadzu model- UV1800 Ssl.no-A116352), stereomicroscope(Labomed SZ-790, slno-97036) and universal testing machine(FSA- TUE-C1000, SR NO- 2009/47),respectively.

Residual monomer evaluation-To determine the unknown quantity of methyl methacrylate leaching in water, a standard graph of methyl methacrylate in distilled water with varied dilutions of 0.1:10, 0.5:10, 0.10:10, 0.15:10, and 0.20:10ml ratio was plotted. After gross finishing, each sample was completely immersed in a screw-capped, amber-colored glass vial containing 10 mL of distilled water for 24 hours. The samples were then removed from the glass vials, and the residual liquid was poured into clear cuvettes. Their residual monomer concentration at 210 nm and the amount of

residual monomer that leached into the distilled water were measured using a UV double beam spectrophotometer. (Figure-1D).

Porosity and flexural strength evaluation -Each sample was trimmed off excess, and 3 indents of dimensions 3mm x 3mm were created at the centre while 2 indents were created at the periphery using a straight-fissure carbide bur. These were examined using a stereomicroscope at 15X magnification. Each surface pore evident in the indented square was counted and added on to other pores evident in the other two squares of the sample to get the final count (Figure-1E). The same samples were subjected to a three-point bending flexural strength test using a universal testing machine with a span length of 50 mm and cross-head speed of 5 mm/min (Figure-1F). The samples were loaded until fracture occurred, and readings were noted.Maximum load obtained was measured in kilonewton (KN) which was converted to Newton (N) and flexural strength was calculated in megapascal (MPa) units according to the formula:$Fs = 3pl/2bd^{2.}$ (where, p = maximum load,l = distance between 2 supports; b = width of specimen; d = thickness of specimen).

Statistical analysis -

Data was compiled and analysed using the statistical software Statistical Package for the Social Sciences (SPSS) version 18.0 (SPSS Inc. Released 2009. PASW Statistics for Windows, Version 18.0. Chicago: SPSS Inc.) and Microsoft Excel. Descriptive statistical measures such as mean, standard deviation, coefficient of variation, and standard error of means were computed for all the study groups. In order to collectively compare the means of the study groups, one-way ANOVA tests were used. The Tukey's

multiple post hoc test was used to compare the test groups in pairs. p-value ≤ 0.05 indicated statistical significance.

RESULTS

The study consisted of 200 acrylic resin samples. Four different curing cycles were used to process 50 samples each (Group I-IV). The experimental procedure is depicted in Figure-1(A-F). Table-1 details the flexural strength, residual monomer content, and porosity values in the four study groups, while Tables-2 and 3 present the comparison of these parameters among the four study groups using one-way analysis of variance (ANOVA) and Tukey's multiple post hoc test, respectively. The mean flexural strength was found to be the greatest in Group I (120.07 ± 6.99 MPa) followed by Group II > Group III > Group IV, with the differences between the groups being statistically significant ($p<0.05$). The mean values of residual monomer content and porosity were found to be the lowest in Group I (0.19 ± 0.03 and 12.28 ± 4.16, respectively) followed by Group II < Group III < Group IV, with the differences between the groups being statistically significant ($p<0.05$).

DISCUSSION

As a base material for dentures, for repairing and relining dentures, and for creating prosthetic teeth, methacrylate resin is widely utilized in dentistry. Methyl methacrylate are leachable from these acrylic denture base materials. Curing cycle has a major role, deciding the physical and mechanical properties of methacrylate resin base materials.

Long curing cycle was found to be associated with the higher flexural strength and lower residual monomer content and porosity in the present study.The current study confirms

the findings of Jerolimov V, who reported that the choice of curing cycle had a greater influence on residual monomer content than the mixing ratio, and that the flexural property of HC DBR material improved with decreasing residual monomer levels.[5]Jadhav et al. discovered, in a manner similar to the present study, that a lengthy curing cycle enabled complete conversion of the monomer to polymer, resulting in enhanced mechanical and physical properties. [4] This is because more cross-linked polymer chains with lower porosity and higher strength were produced as a result of longer processing at higher temperatures, which were also linked to more benzoyl peroxide breakdown to form free radicals.[3,4,6]In contrast to the current study, they also reported that the lack of terminal boiling resulted in an increased residual monomer content. [4] In the case of quick curing, Craig et al. hypothesised that molecular mobility increased with rising temperature and terminal boiling, resulting in more thorough polymerization and less residual monomer content. These results are in line with the findings of the current investigation, which showed that in DBR produced with quick curing cycles, longer terminal boiling periods were related to improved physical and mechanical properties. [2]

Villittu et al. came to the conclusion that the residual monomer levels of denture base polymers were considerably impacted by the polymerization temperature and time. [7] Even though it was used to reduce time, the rapid polymerization cycle was ineffective in producing complete polymerization and reducing residual monomer levels, which had a negative impact on the mechanical qualities. Additionally, the unreacted monomers acted as plasticizers to weaken the polymer by lowering the interchange forces, which made deformation under load easier to happen.[7] It has been suggested that the leftover

monomer that diffuses from acrylic resin acts as the main irritant and sensitizer that might trigger an allergic eczematous reaction on the skin and oral mucosa. [8] These findings are also consistent with the literature of Phoenix et al.[9]Of the various techniques available to detect the content of residual monomer in acrylic resins (such as infrared spectroscopy, gas chromatography, gas-liquid chromatography, high-performance liquid chromatography), UV spectrophotometry technique has been used in this present study as it is a precise and simple method. When exposed to the UV and visible spectrum, the UV double-beam spectrophotometer absorbs some of the light. The concentration of the liquid substance can be determined by measuring this.[10,11]

Despite the several commercially available polymerization activators, there remains some residual monomer after the transformation of methyl methacrylate to polymethyl methacrylate. The cytotoxicity of acrylic denture bases is also significantly influenced by storage, with the cytotoxicity being highest in the first 24 hours following polymerization and decreasing proportionately with extended immersion in water, regardless of the DBR material. [12,13] As a result, all of the samples were submerged in distilled water for 24 hours prior to the present study's examination of the amount of residual monomer. Braun et al. showed that greater hardness values found after storage in water were caused by leaching of residual monomer from denture base material.[14] Hence, the samples evaluated for residual monomer content were not used to determine flexural strength as they could yield false positive results.[14]

The flexural strength observed in the present study resonated with the findings of Jerolimov V.[5] However, Islam et al reported that no significant difference was seen in

the flexural strength of HC acrylic DBR cured at 100°C for different periods of time (at 20, 40 and 60 minutes).[15]

Porosities in the material's matrix not only weaken the denture base and cause high internal stresses, but they also serve as sites for crack nucleation and propagation.[16] They also have a negative impact on physical and mechanical properties, as well as aesthetics, with the possibility of fluid retention and microbial colonisation.[16] Of the various methods available for porosity detection and measurement (such as optical microscope, scanning electron microscope and Boley's gauge), stereomicroscope with 15X magnification has been employed in the present research due to its feasibility and three-dimensional visualization of the sample, which was in accordance with the study conducted by Badr et al.[17] Porosities in all the samples were examined at 5 different indented areas for the purpose of standardization and evaluation of different portions of the samples.

When compared to long and short curing cycles, ultrashort curing cycles significantly reduced mechanical properties. However, if both the dentist and the patient are short on time, they may be considered for prosthesis fabrication. However, because this study may not be entirely representative of intraoral conditions, more clinical studies are needed to produce clinically significant results. [17]

As a result, the current research shows that curing temperature and time have a significant impact on the mechanical and physical properties of HC PMMA. However, because it is a single-center, in-vitro study with a small sample size, this study has limitations. Multicentric, long-term, prospective clinical studies with a larger sample size can overcome these challenges.

CONCLUSION

Curing temperature and time have a significant effect on the mechanical and physical properties of HC PMMA. Long curing cycle (9 hours at 74°C) is associated with the higher flexural strength and lower residual monomer content and porosity compared to short curing cycles with bench curing.

REFERENCES

1. Phillips RW, editor. Skinner's Series of Dental Materials, 7th edition. Philadelphia: W. B. Saunders Co; 1973.
2. Craig RG, Powers JM, editors. Restorative Dental Materials, 11th edition. St. Louis, MO: Mosby, Inc.; 2002.
3. Vallittu PK, Miettinen V, Alakuijala P. Residual monomer content and its release into water from denture base materials. Dent Mater 1995;11(6):338-42.
4. Jadhav R, Bhide SV, Prabhudesai PS. Assessment of the impact strength of the denture base resin polymerized by various processing techniques. Indian J Dent Res 2013;24(1):19-25.
5. Jerolimov V. The effect of variations in the polymer/monomer mixing ratios on residual monomer levels and flexural properties of denture base materials. Quinte Dent Tech 1985;9:431-34.
6. Nisar S, Moeen F, Hasan U. Effect of varying curing regimes and powder-liquid ratios on the flexural strength and surface porosities of heat cure acrylic: an in-vitro experiment. International Journal of Dental Sciences and Research 2015;3(3):64-71.

7. Vallittu PK. Ruyter IE, Buykuilmaz S. Effect of polymerization temperature and time on the resisual monomer content of denture base polymers. Eur J Oral Sci 1998;106:588-93.
8. Jorge JH, Giampaolo ET, Machado AL, Vergani CE. Cytotoxicity of denture base acrylic resins: a literature review. J Prosthet Dent 2003;90(2):190-3.
9. Phoenix RD, Mansueto MA, Ackerman NA, Jones RE. Evaluation of mechanical and thermal properties of commonly used denture base resins. J Prosthodont 2004;13(1):17-27.
10. Ayaz EA, Durkan R, Koroglu A, Bagis B. Comparative effect of different polymerization techniques on residual monomer and hardness properties of PMMA-based denture resins. J Appl BiomaterFunct Mater 2014;12(3):228-33.
11. Rao MRN, Reddy NS, Ramasamy C, Banu RF. Spectrophotometric analysis of residual monomer in acrylic resin samples processed with two different polymerization methods. Indian J Dent Sci 2016;8(1):35-7.
12. Ivković N, Božović D, Ristić S, Mirjanić V, Janković O. The residual monomer in dental acrylic resin and its adverse effects. Contemporary Materials 2013;4(1):84-91.
13. Sheridan PJ, Koka S, Ewoldsen NO, Lefebvre CA, Lavin MT. Cytotoxicity of denture base resins. Int J Prosthodont 1997;10;73-7.
14. Braun KO, Mello JA, Rached RN, Del Bel Cury AA. Surface texture and some properties of acrylic resins submitted to chemical polishing. J Oral Rehab 2003;30(1):91-8.

15. Islam KZ, Moral MAA, Rahman MM. Effect of curing time on the flexural strength of heat cured acrylic resin. City Dental College J 2012;9(2):15-19.
16. Compagnoni MA, Barbosa DB, de Souza RF, Pero AC. The effect of polymerization cycles on porosity of microwave-processed denture base resin. J Prosthet Dent 2004;91(3):281-5.
17. Badr NA, Ibrahim AM, Mohamed GF. Effect of the curing mode on the clinical performance and properties of acrylic resin overdenture bases. Cairo Dent J 2008;2(24):259-71.

LEGENDS

Table-1: Flexural strength, residual monomer content and porosity values in the four study groups

Table-2: Comparison of different parameters among the four study groups using one-way analysis of variance (ANOVA)

Table-3: Pair wise comparison of different parameters among the four study groups using Tukey's multiple post hoc test

Figure-1: The experimental procedure

Figure-1: The experimental procedure

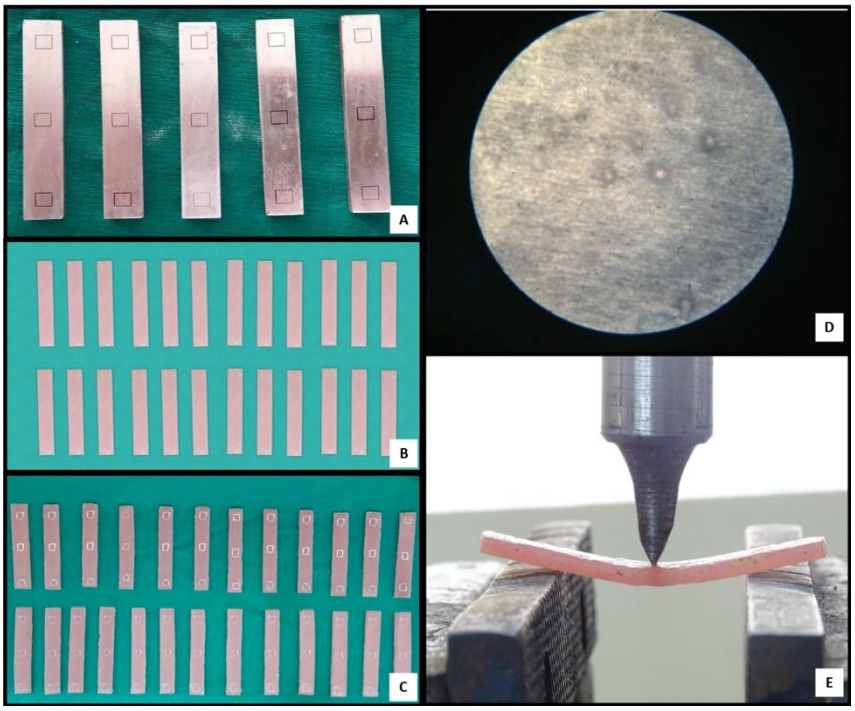

Figure-1: (A) Standard sized metal dies; **(B)** Acrylic resin samples; **(C)** Acrylic samples for porosity evaluation; **(D)** Porosity examination by stereomicroscope; **(E)** Sample testing by universal testing machine.

Table-1: Flexural strength, residual monomer content and porosity values in the four study groups

Parameter	Groups	Mean ± SD	Standard error	Coefficient of variation
Flexural strength (in MPa)	**I**	120.07 ± 6.99	1.40	5.82
	II	106.75 ± 7.65	1.53	7.16
	III	83.01 ± 4.44	0.89	5.35
	IV	78.37 ± 4.96	0.99	6.33
Residual monomer content	**I**	0.19 ± 0.03	0.01	17.16
	II	0.29 ± 0.04	0.01	13.93
	III	0.44 ± 0.04	0.01	8.70
	IV	0.50 ± 0.03	0.01	6.44

Porosity	**I**	12.28 ± 4.16	0.83	33.86
	II	17.92 ± 4.03	0.81	22.49
	III	31.60 ± 5.69	1.14	17.99
	IV	34.60 ± 7.01	1.40	20.27

table-2: Comparison of different parameters among the four study groups using one-way analysis of variance (ANOVA)

Parameter	**Source of variation**	**Degrees of freedom**	**Sum of squares**	**Mean sum of squares**	**F-value**	**p-value**
Flexural strength (in MPa)	Between groups	3	29246.47	9748.8242	257.1259	0.0001*
	Within groups	96	3639.80	37.9146		
	Total	99	32886.27	-		
Residual monomer content	Between groups	3	1.52	0.5060	384.7083	0.0001*
	Within groups	96	0.13	0.0013		
	Total	99	1.64	-		
Porosity	Between groups	3	8610.12	2870.0400	99.7957	0.0001*
	Within groups	96	2760.88	28.7592		
	Total	99	11371.00	-		

*Abbreviations: *Significant at 5% level of significance*

Table-3: Pair wise comparison of different parameters among the four study groups using Tukey's multiple posthoc test

Parameter	**Groups**	**I**	**II**	**III**	**IV**
Flexural strength (in MPa)	Mean	120.07	106.75	83.01	78.37
	SD	6.99	7.65	4.44	4.96
	Group I	-			
	Group II	p=0.0001*	-		
	Group III	p=0.0001*	p=0.0001*	-	
	Group IV	p=0.0001*	p=0.0001*	p=0.0447*	-
Residual	Mean	0.19	0.29	0.44	0.50

monomer content	SD	0.03	0.04	0.04	0.03
	Group I	-			
	Group II	p=0.0001*	-		
	Group III	p=0.0001*	p=0.0001*	-	
	Group IV	p=0.0001*	p=0.0001*	p=0.0001*	-
Porosity	Mean	12.28	17.92	31.60	34.60
	SD	4.16	4.03	5.69	7.01
	Group I	-			
	Group II	p=0.0020*	-		
	Group III	p=0.0001*	p=0.0001*	-	
	Group IV	p=0.0001*	p=0.0001*	p=0.2036	-

*Abbreviations: *Significant at 5% level of significance*