Original Article

pISSN, eISSN 0125-5614
M Dent J 2019; 39 (1) : 9-14

Curing process modification of a 'self-cured' injection molding material: Effect on surface hardness

Kunwadee Choedkiatsakun, Amornrat Wonglamsam*, Widchaya Kanchanavasita

Department of Prosthodontics, Faculty of Dentistry, Mahidol University, Thailand

Objectives: The objective of this study was to compare the surface hardness of a self-cured injection-molding denture base material, which its curing process was modified from that recommended by the manufacturer, when stored in water at 7 days and 30 days.

Materials and Methods: Ten rectangular specimens (10 mm x 64 mm x 2.5 mm) in three groups of injection-molding denture base materials were prepared from separate mix. The first group contained SR Ivocap® High Impact heat-cured specimens which were polymerized in water at 100°C according to the manufacturer's instruction (Ivocap wet curing). The second group was IvoBase® Hybrid self-cured injection-molding specimens which were polymerized via the injection machine at 40°C up to120°C (IvoBase dry curing). The third group was IvoBase® Hybrid specimens which were mixed according to the manufacturer's instruction but the processing method was the same as Ivocap wet curing. The Vickers hardness of the specimens were measured at 7 and 30 days of water storage. Split-plot ANOVA was used to analyze the data at α=0.05.

Results: The surface hardness of IvoBase® Hybrid when polymerized according to the manufacturer's instruction and when polymerized with a modified method were not significantly different at both 7 days and 30 days storage in water. The surface hardness of IvoBase® Hybrid was significantly higher than that of SR Ivocap® High Impact. The hardness of IvoBase® Hybrid significantly increased when they were stored in water for a longer time from 7 days to 30 days. The surface hardness of SR Ivocap® High Impact significantly decreased with water storage from 7 days to 30 days.

Conclusions: The modified curing technique of IvoBase® Hybrid did not alter the surface hardness characteristics of the material. Time of storage in water had an effect on the material's hardness differently. The hardness of the self-cured material increased with increasing storage time from 7 days to 30 days, whereas the hardness of the heat-cured material decreased.

Keywords: Injection molded acrylic resin, surface hardness, denture base material, acrylic resin.

How to cite: Choedkiatsakun K, Wonglamsam A, Kanchanavasita W. Curing process modification of a 'self-cured' injection molding material: Effect on surface hardness. Mahidol University. M Dent J 2019; 39: 9-14.

Introduction

Poly(methyl methacrylate) or PMMA is the material mostly used for fabrication of dental prostheses. The compression molding technique has been applied to fabricate the denture for many years. However, the main disadvantage of this technique is the polymerization shrinkage. Recently, the injection molding technique has become more attractive. This technique provides accurate dimension, less skin sensitivity from direct contact with monomer during manipulation and less processing time and cost. [1-3] Many studies reported that different processing technique and polymerization process may provide different mechanical properties such as flexural strength, micro roughness, bond strength and hardness. [4, 5]

Correspondence author: Amornrat Wonglamsam
Department of Prosthodontics, Faculty of Dentistry, Mahidol University, Thailand
6 Yothi Road, Ratchathewi District Bangkok 10400 Thailand
Tel: 022007817-8 Email: amornrat.won@mahidol.ac.th
Received : 10 September 2019 Accepted : 11 February 2019

Auto-polymerizable materials is seldom used for definitive denture fabrication because they have lower mechanical properties than the heat-polymerizable materials. Ali et al. reported that heat-polymerizable material provided higher surface hardness than auto-polymerizable material. [6]

Hardness of material indicates its resistance to localized plastic deformation induced by either mechanical indentation or abrasion such as brush polishing and food stimulating. It may also be used to predict the amount of residual monomer content in the polymerized resin and to evaluate the conversion degree of dental polymers. The hardness is hence, usually used to predict the longevity of denture base material. [1, 7-9] Low degree of conversion results in high residual monomer. The residual monomer molecules act as plasticizer that causes the reduction of surface hardness. The hardness can be used to evaluate the polymerization depth of resin-based materials and the conversion degree of conventional heat-polymerizing and auto-polymerizing acrylic resins. [10]

Neppelenbroek et al. found that heat-polymerizable materials fabricated by compression molding technique provided high surface hardness because of the residual monomer molecules reduction after water storage. [10] In addition, Rajaee et al. mentioned that the hardness of heat-polymerizable materials denture base was higher than the hardness of auto-polymerizable materials denture base. [5]

Auto-polymerizable materials have curing temperature less than 65°C. [11] Heat less than 100°C may cause higher methyl methacrylate contents in polymers than heating cycles with temperatures 100°C. It was also found that the amount of residual monomer reduced when the curing temperature increased. Therefore, the cytotoxic effects of auto-polymerized acrylic resins may be decreased by heat-treatment. [12]

The polymerization technique of injection molding material is different depending on the manufacturer. [13, 14] IvoBase® Hybrid system specially designs the automated IvoBase® Injector machine which initially polymerizes the IvoBase® Hybrid material from 40°C , total curing time is 35 minutes. [14] IvoBase® Hybrid material is classified as an auto-polymerizable material by the manufacture. [14] Initial curing temperature of IvoBase® Hybrid material by automated IvoBase® injector machine is lower than that of heat-cured material. Ivocap® High Impact is heat-cured injection molding material. Curing temperature of this material is 100°C for 35 minutes.

A few research reported the surface hardness of auto-polymerizable and heat-polymerizable injection molding materials and effects on their surface hardness. Therefore,the objective of this study was to investigate the effect of curing process on surface hardness of the two types of injection-molding materials, after 2 periods of water storage. The water storage for 7 days was the standard immersion time according to ISO specification 20795-1:2013, [11] for 30 days was represented for longer immersion time than standard. The materials used in this work were Ivocap® High Impact which is a heat-cured material and IvoBase® Hybrid which is classified as an auto-polymerizable material by the manufacturer. [13, 14] The curing process of IvoBase® Hybrid was modified from that recommended by the manufacturer to resemble that of the general heat-cured material. It was expected that alternative method of curing would increase its surface hardness.

Materials and methods

Two commercial injection molded acrylic resins products, one was a self-cured and the other was heat-cured, were used in this investigation. The manipulation and processing procedures are presented in Table 1.

Table 1 Material used in this investigation

Material	Processing	Measurement Powder:liquid
SR Ivocap® High Impact (Group 1-Ivocap wet curing)	Place mold in water, heat up to 100°C and boil it for 35 minutes. Then cool in cold water for 30 minutes.	20 g : 30 ml
IvoBase® Hybrid (Group 2-IvoBase dry curing)	Dry curing following the program in the automated injection unit: initial cure at 40°C then at 120ºC, total curing time 35 minutes. Then cool in cold water for 15 minutes.	34 g: 20 ml
IvoBase® Hybrid (Group 3-IvoBase wet curing)	Place mold in water, heat up to 100°C and boil it for 35 minutes. Then cool in cold water for 30 minutes.	34 g: 20 ml

Ten rectangular specimens (10 mm x 64 mm x 2.5 mm) in three groups of injection-molding denture base materials were prepared using a mold from separate mix. The mold was placed on the gypsum dental stone type 3 in the dental flask. The resin was mixed and packed to the mold following the manufacturer's instructions. [13, 14] For Group 3 IvoBase® Hybrid was mixed according to manufacturer's instruction but processing method resembled that of the heat-cured Ivocap® High Impact (Group 1). All specimens were polished with standard metallographic paper: p150, 300, 600, 1000, 1200, 1500, and 2000. The specimens were immersed in 37°C distilled water until the time required for surface hardness measurement.

After 7 days water storage, each specimen was removed from water and immediately tested for Vickers hardness at room temperature using a micro-hardness tester (Future-Tech Corp FM-700, Tokyo, Japan) with applied loading of 300 grams for 15 second. [6] Six indentations were made at different points along the specimen. The two diagonals length of the indentation were measured and calculated the value of the hardness by using the following formula;

HV (Vickers hardness) = $1.854\frac{F}{d^2}$

F represents load in Kg, d arithmetic mean of the two diagonals, d_1 and d_2, in mm

The hardness values from six indentations of each specimen were averaged to obtain the means hardness value at 7 days immersion. After that all specimens were re-immersed in distilled water until 30 days. The hardness of each specimen was remeasured at six different positions (2mm next to the previous position). The hardness values from six indentations of each specimen were averaged to obtain the means hardness value at 30 days immersion. The hardness data in each group was tested for normal distribution by Shapiro-Wilk test. (α=0.05). Split-plot ANOVA was used to compare the statistical difference of the hardness value at α=0.05.

Results

Means and standard deviations (SD) of Vickers hardness are shown in Table 2.

From Table 2, the surface hardness of IvoBase® Hybrid (Group 2 and 3) was significantly higher than that of SR Ivocap® High Impact (Group 1) ($p<0.05$). The surface hardness of IvoBase® Hybrid (Group 2) when polymerized according to the manufacturer's instruction and when polymerized with a modified method (Group 3) were not significantly different at both 7 days and 30 days storage in water ($p>0.05$). The hardness of IvoBase® Hybrid significantly increased when they were stored in water for a longer time from 7 days to 30 days ($p<0.05$). The surface hardness of SR Ivocap® High Impact significantly decreased with water storage from 7 days to 30 days ($p<0.05$).

Table 2 Means and standard deviations of surface hardness of 3 experiment groups at 2 water immersion periods (n=10)

Materials		Surface Hardness (HV)	
		7 days in water	30 days in water
		Mean ± SD	Mean ± SD
Group 1	SR Ivocap® High Impact (wet curing)	13.3 ± 0.2 $^{A, a}$	12.8 ± 0.4 $^{B, c}$
Group 2	IvoBase® Hybrid (dry curing)	16.7 ± 0.4 $^{C, b}$	17.5 ± 0.5 $^{D, d}$
Group 3	IvoBase® Hybrid (wet curing)	16.8 ± 0.2 $^{E, b}$	17.1 ± 0.3 $^{F, d}$

Note:

:within the same group (horizontal row), means with different superscripts written in uppercase letters were significantly different ($p < 0.05$).

:within the same water storage period (vertical column), means with different superscripts written in lowercase letters were significantly diffirent ($p< 0.05$)

Discussion

Auto-polymerizable materials were reported to have lower mechanical properties than heat-polymerizable materials. [2, 6] They also have higher residual monomer content than heat-polymerized resins since high curing temperature of the heat-polymerized resins causes the mobility of the molecular chains and enhances the conversion of monomer into polymer. Heating cycles with temperatures less than 100°C may result in higher residual methyl methacrylate contents in polymers than heating cycles with temperatures 100°C.

Ivoclar Vivadent company claimed that self-cured IvoBase® Hybrid provided high degree of monomer conversion during polymerization process using their automated injection unit. IvoBase® Hybrid material is classified as an auto-polymerizable material according to the ISO 20795-1:2013 Dentistry - Base polymers - Part 1: Denture base polymers, which stated the polymerization temperature lower than 65 °C. The claimed quality of the material is equivalent to or even exceeds that of heat-polymerizable materials. This might be because it contains a heat initiator such as benzoyl peroxide. Moreover, after an initial cure at 40°C the curing temperature is raised up to 120°C. The manufacturer claimed that the residual monomer content is less than 1.5% (limit values according to ISO 20795-1 is 4.5% for auto-polymerizable material). The residual monomer content can be reduced to below 1% by activating residual monomer reduction function. [13] This function extends the polymerization time results in the additional monomer conversion. Reduction of residual monomer may increase some mechanical properties of material. It was found from this study that the surface hardness of IvoBase® Hybrid were significantly higher than that of Ivocap® High Impact heat-cured material at 7 days and 30 days immersion in water (Table 2). This might be because of the reduction of residual monomer which needs to be confirmed in further study.

Okuyama et al. found that the materials with higher powder to liquid ratio (P/L ratio) exhibited higher flexural strength. [15] Arora et al. reported that the materials with higher P/L ratio exhibited higher values of hardness and flexural strength when compared to materials with lower P/L ratio. The P/L ratio may have an effect on hardness of the material [16]; increasing powder to liquid (P/L) ratio causes a closer three-dimensional network structure and decreases the quantities of the unreacted monomer. On the other hand, lower P/L ratio will cause the higher levels of residual monomer which eventually results in excessive leaching of residual monomer, which in turn results

in higher number of void formation in the resin. There is a parallel relationship between the level of residual monomer and the percentage of water sorption as suggested by Dogan et al. [17]. Therefore, the IvoBase® Hybrid which has the higher P/L ratio than SR Ivocap® High Impact will provide the higher hardness.

In this study, the hardness of IvoBase wet curing (Group 3) was not significantly different form that of IvoBase dry curing in the automated injection unit (Group 2) in all period of investigation. This might be because the IvoBase dry curing has final curing temperature up to 120°C that improves the properties of material. This final cure temperature is more than that of the 100°C heat polymerization process (wet curing). It can be concluded that the processing technique provided by the manufacturer is the best method. Apart from using the expensive curing unit, this curing method is more convenient, easy to use, and less time consuming.

The Ivoclar Vivadent Company did not provide the detail of their materials compositions such as type of the initiator. It is interesting to find out in the future what the initiator they use in their materials. According to the study of Rajaee et al., they found that using copper and barbituric acid ions as a replacement for tertiary amine leads to a reduction in the amount of residual monomer in this resin. [5]

Many researches concluded that the reduction of residual monomer results in the mechanical properties improvement and decreases water absorption. It was found that increasing the curing time and temperature can decrease the residual monomer, resulting in the improvement of tensile strength and reduction of water absorption. [12, 17]

The results of this study showed that the hardness of IvoBase® Hybrid significantly increased when increased water storage periods from 7 days to 30 days (Table 2). The increase of the hardness might occur from the releasing of the less residual monomer and low water sorption. [17] The residual monomer acts as plasticizer which decrease material's hardness. [20] Braun et al. found that leaching of residual monomer from auto-polymerizable materials (Jet-Clá ssico) resulted in the higher surface hardness. [21] Moreover, Moradians et al. observed that the hardness of auto-polymerizing resin increased after 1 month of water storage. The hardness also continuously increased over 2- month storage period. [22] Neppelenbroek found that the hardness of both heat polymerizable materials (Lucitone 550, QC-20) gradually increased over 60 days of water storage. However, the hardness after 60, 90, and 120 days of water storage were not significantly different. [10] It was found from the literature that the hardness increased until water storage for 2 months. However, the water storage period of 30 days was investigated in this study. The effects of the residual monomer content on the hardness of IvoBase dry curing and wet curing after long period of water storage more than 30 days should be investigated in further study.

From this study, when the water storage period increased from 7 days to 30 days, the hardness of Ivocap wet curing significantly decreased. This might be from the releasing of the high residual monomer and high water sorption. [17] Acrylic resin which is a polar material, totally absorbs water by diffusion. Water molecules act as a plasticizer, the flow of long-chain polymers can be facilitated. This might cause the reduction of hardness and affects other mechanical properties. [5, 23]

This study is preliminary research which investigated surface hardness from two water storage times, at 7 days as standard immersion time according to ISO specification 20795-1:2013 and at 30 days. For further study of surface hardness, it should evaluate at least three proper water storage times.

It can be concluded from the results that the types of material (IvoBase® Hybrid and SR Ivocap® High impact) and water storage period affect the hardness value.

References

1. Bahrani F, Safari A, Vojdani M, Karampoor G, Patil S. Comparison of hardness and surface roughness of two denture bases polymerized by different methods. ***World J Dent*** 2012; 3:171-5.
2. Parvizi A, Lindquist T, Schneider R, Williamson D, Boyer D, Dawson DV. Comparison of the dimensional accuracy of injection-molded denture base materials to that of conventional pressure-pack acrylic resin. ***J Prosthodont*** 2004; 13: 83-9.
3. Nogueira SS, Ogle RE, Davis EL. Comparison of accuracy between compression- and injection-molded complete dentures. ***J Prosthet Dent*** 1999; 82: 291-300.
4. Lira AF, Consani RL, Mesquita MF, Nobilo MA, Henriques GE. Effect of toothbrushing, chemical disinfection and thermocycling procedures on the surface microroughness of denture base acrylic resins. ***Gerodontology*** 2012; 29: e891-7.
5. Rajaee N, Vojdani M, Adibi S. Effect of food simulating agents on the flexural strength and surface hardness of denture base acrylic resins. ***OHDM*** 2014; 13: 1041-7.
6. Ali IL, Yunus N, Abu-Hassan MI. Hardness, flexural strength, and flexural modulus comparisons of three differently cured denture base systems. ***J Prosthodont*** 2008; 17: 545-9.
7. Anusavice KJ, Shen C, Rawls RH. Phillips' Science of Dental Materials. 12 th ed. St. Louis: Elsevier; 2012.
8. Farina AP, Cecchin D, Soares RG, Botelho AL, Takahashi JM, Mazzetto MO, et al. Evaluation of Vickers hardness of different types of acrylic denture base resins with and without glass fibre reinforcement. ***Gerodontology*** 2012; 29: e155-60.
9. McCabe JF, Walls AWG. Applied Dental Materials. 9 th ed. Oxford: Wiley-Blackwell; 2008.
10. Neppelenbroek KH, Pavarina AC, Vergani CE, Giampaolo ET. Hardness of heat-polymerized acrylic resins after disinfection and long-term water immersion. ***J Prosthet Dent*** 2005; 93: 171-6.
11. International Organization for Standardization. ISO 20795-1 Dentistry-Base polymers Part 1: Denture base polymers. Geneva, Switzerland ; 2013.
12. Ivkovic N, Bozovic D, Ristic S, Mirjanic V, Jankovic O. The residual monomer in dental acrylic resin and its adverse effects. ***Contemp Mater*** 2013; 1: 85-91.
13. SR Ivocap® System 2016. Available from: http://www.ivoclarvivadent.us/en-us/p/laboratory-professional/products/removable-denture-prosthetics/materials-for-dentures/sr-ivocap-heat-cure-polymer.
14. IvoBase® System 2016. Available from: https://www.ivoclarvivadent.us/explore/sr-ivobase.
15. Okuyama Y, Shiraishi T, Yoshida K, Kurogi T, Watanabe I, Murata H. Influence of composition and powder/liquid ratio on setting characteristics and mechanical properties of autopolymerized hard direct denture reline resins based on methyl methacrylate and ethylene glycol dimethacrylate ***Dent Mater J*** 2014; 33: 522-9.
16. Arora S, Arora A, Upadhyaya V, Goyal A. Evaluation of the mechanical properties of high impact denture base resin with different polymer to monomer ratios: An In vitro study. ***Indian J Dent Sci*** 2017; 9: 67-72.
17. Dogan A, Bek B, Cevik NN, Usanmaz A. The effect of preparation conditions of acrylic denture base materials on the level of residual monomer, mechanical properties and water absorption. ***J Dent*** 1995; 23: 313-8.
18. Bural C, Aktas E, Deniz G, Unlucerci Y, Kizilcan 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. ***Dent Mater*** 2011; 27: 1135-43.
19. Lung CY, Darvell BW. Minimization of the inevitable residual monomer in denture base acrylic. ***Dent Mater*** 2005; 21: 1119-28.
20. 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: 179-83.
21. 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: 91-8.
22. Moradians S, Fletcher AM, Amin WM, Ritchie GM, Purnaveja J, Dodd AW. Some mechanical properties including the repair strength of two self curing acrylic resins. ***J Dent*** 1982; 10: 271-80.
23. Chandu GS, Asnani P, Gupta S, Khan FM. Comparative evaluation of effect of water absorption on the surface properties of heat cure acrylic: An in vitro study. ***J Int Oral Health*** 2015; 7: 63-8.