

INFLUENCE OF THE POLYMERIZATION CYCLE ON THE FLEXURAL STRENGTH OF FOUR DIFFERENT PMMA-BASED HEAT-POLYMERIZED DENTURE BASE RESINS.

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Abstract

Purpose: PMMA-based heat-polymerized acrylic resins used in the fabrication of denture bases may be cured in different ways. As the polymerization cycle length affects fabrication costs and time, a fast cycle is more advantageous. However, polymerization cycles may influence mechanical properties.

Objective: The purpose of this study was to evaluate the influence of the polymerization cycle on the flexural strength of four types of PMMA-based heat-polymerized resins used as denture base materials.

Materials and methods: The ISO Standard 1567:1999 (Dentistry - Denture base material) was followed in specimen preparation and flexural strength testing of four types of PMMA-based heat-curing resins: Characterized Lucitone (Dentsply-DeTrey); Paladon 65 (Heraeus Kulzer); ProBase Hot (Ivoclar-Vivadent); Prothyl Hot (Zhermack). Resin specimens were obtained following different curing cycles: Standard and Slow for Lucitone; Fast, Standard, and Slow for Paladon 65; the five variants defined by the manufacturer for ProBase Hot; the Standard cycle for Prothyl Hot. For each polymerization cycle six specimens (64 ± 1) mm in length, ($10 \pm 0,2$) mm in width, and ($3,3 \pm 0,2$) mm in height, were prepared. For flexural strength measurements each specimen was loaded until failure with a new testing device (Flexural Test Rig), developed following the indications of ISO 1567:1999. The flexural strength was calculated in MPa and the values were compared with ANOVA and Tukey's test for post-hoc ($p = 0.05$).

Results: The polymerization cycle has no or minimal influence on the flexural strength of the tested resins. Lucitone exhibited relatively low resistance to flexural loads as when compared with the other resins (Group 7: $78,467 \pm 5,623$ MPa; Group 8: $71,198 \pm 3,775$ MPa).

Conclusion: With regard to flexural strength, a slow curing cycle does not appear to be justified for the either Lucitone or ProBase Hot, whereas slow polymerization may be advisable for Paladon 65 tested resins, whereas the fast curing cycle V3 was the most favourable to achieve the optimal flexural strength for ProBase Hot.

Introduction

Polymers most commonly used as denture base materials are PMMA-based heat-polymerized acrylic resins¹. While this type of resin is easy to handle and requires simple application for forming and processing, a common problem in upper and lower complete dentures is the midline fracture of the prosthesis^{2,3}. The primary cause of this failure, with the exception of accidental damage, is flexural fatigue stress exerted by repeated masticatory forces^{4,5}. A factor that can accelerate the initiation and the propagation of surface cracks

is the presence of labial and lingual frenums^{3,6}. The base has to be shaped to accommodate the frenum, and a deep notch can promote stress concentration⁷. To improve mechanical properties, the chemical composition of a resin can be modified or reinforced with high-resistance fibers, thus obtaining a so-called "high-impact" resin^{8,23}.

Several acrylic resins are currently available on the market for the fabrication of denture bases. Each manufacturer has recommended different polymerization cycles. According to them, variations among the different polymerization modes may include temperature and storage time. To save time, a rapid polymerization mode would obviously be preferable. However, it has been demonstrated that the type of polymerization cycle affects the residual monomer content^{24,25}, an important parameter in determining the mechanical

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Table. 1 - Polymerization cycle of each resin

T_0 : start temperature of water;
 T_1 and T_2 : temperatures of water during the polymerization cycles;
 t_0 , t_1 and t_2 : the maintaining time at relative temperatures

Group	Resin	Abbr	Cycle	T_0	t_0	T_1	t_1	T_2	t_2
1	ProBase Hot	PBH	Standard	23°C	0 min	100°C	45 min	-	-
2			V1	23°C	0 min	70°C	1 h	100°C	30 min
3			V2	70°C	1 h	100°C	30 min	-	-
4			V3 Fast	100°C	0 min	100°C	40 min	-	-
5			Slow	23°C	0 min	80°C	10 h	-	-
6	Prothyl Hot	PTH	Standard	60°C	0 min	100°C	30 min	-	-
7	Characterized Lucitone	CLT	Standard	73°C	1,5 h	100°C	30 min	-	-
8			Slow	73°C	9 h	-	-	-	-
9	Paladon 65	P65	Fast	80°C	15 min	100°C	20 min	-	-
10			Standard	37°C	0 min	70°C	30 min	100°C	30 min
11			Slow	23°C	0 min	90°C	10 h	-	-

properties of the resin^{26,27}, and which also has a bearing on polymer cytotoxicity²⁸.

The aim of this study was to evaluate the influence of the polymerization cycle on the flexural strength of four different heat-polymerizable PMMA-based polymers.

The null hypotheses tested were (1) there is no statistically significant difference among the final flexural strengths of the different resins and (2) the polymerization cycle has no influence of the final flexural strength of the resins.

Materials and Methods

The European Standard I567:1999 (Dentistry - Denture Base Polymers) was followed in performing this study. Four resins were selected:

ProBase Hot (PBH) - (Ivoclar Vivadent AG, Schaan, Liechtenstein)

Prothyl Hot (PTH) - (Zhermack, Badia Polesine, Rovigo, RO, Italy)

Characterized Lucitone (CLT) - (Dentsply DeTrey GmbH, Hanau-Wolfgang, Germany)

Paladon 65 (P65) - (Heraeus Kulzer GmbH & Co. KG, Hanau, Germany)

Table 1 reports the different experimental groups, showing the resins tested and their respective evaluated polymerization cycles. Six specimens were prepared for each experimental group. From the 4 different resins, a total of 11 polymerization cycles were obtained. For each of the 11 reported cycles, 6 specimens were necessary. Therefore 66 tests were performed in total.

To obtain a suitable mould, two stainless steel metal models of the specimen plate (65 mm x 40 mm x 5 mm) were made

and verified with a manual caliper with an accuracy of 0,1 mm. Each metal model was invested in a denture flask, so that the corners were not less than 5 mm from the walls (Fig. 1). An addition reaction silicone (Platinum 95, Zhermack, Badia Polesine, Rovigo, RO, Italy) was used. Two flasks were filled using type III gypsum (Dental Hydrocall, KerrLab, Orange, CA, U.S.A.). After removing the metal model, a gypsum-resin insulator was applied on the gypsum as indicated in the manufacturer’s instructions for each resin (Table 2). The liquid (monomer) was poured in the manufacturer’s mixing cup and was saturated with the powder (polymer). The dough was mixed manually with a spatula for 30 sec by the same operator, after which the cup was corked according to the manufacturer’s instructions. The resin was placed manually in the mould and a poly-ethylene sheet interposed between the

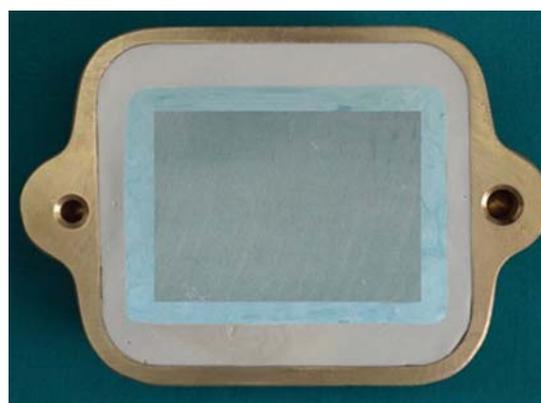


Fig. 1 - The metal model invested in the denture flask

Table 2 - Gypsum/resin insulators.

Resin	Insulator
PBH	Separating Fluid, Ivoclar Vivadent AG, <i>Schaan, Liechtenstein</i>
PRH	Zhermack, <i>Badia Polesine, Rovigo, RO, Italy</i>
CLT	Al-Cote Separating Agent, Dentsply DeTrey GmbH, <i>Hanau-Wolfgang, Germany</i>
P65	Aislar Separating Fluid, Heraeus Kulzer GmbH & Co. KG, <i>Hanau, Germany</i>

two parts of the flask. The flask was closed and placed in the hydraulic press at a 20 bar pressure for 5 sec; it was then opened to remove the excess resin with a blade. This procedure was repeated under a 40 bar pressure. Subsequently, the poly-ethylene sheet was removed and the flask locked and placed in the hydraulic press under a 80 bar pressure. After 10 min the flask was placed in the water polymerizer (Acrydig 4, F.lli Manfredi S.p.a., *San Secondo di Pinerolo, TO, Italy*).

Every polymerization cycle suggested by the manufacturer was performed on each resin. Using two flasks simultaneously, it was possible to obtain two resin plates, 65 mm in length, 40 mm in width, and 5 mm in height. Each resin plate was ground and polished, first with pumice and a wet muslin wheel and then with a polishing compound. Each resin plate was cut lengthwise (Isomet 1000, Buehler, *Lake Bluff, IL, U.S.A.*) into three equal strips measuring 65 mm long and 10,5 mm wide. The strips were machined and wet-ground with metallographic paper at 600 and 1200 FEPA, until the required dimensions of 64 ± 1 mm in length, $10,0 \pm 0,2$ mm in width and $3,3 \pm 0,2$ mm in height were obtained. The specimens were verified with a digital caliper with an accuracy of $\pm 0,01$ mm (Digital Caliper, Orteam S.r.l., *Milan, MI, Italy*) and numbered prior to water storage at 37°C for 50 ± 2 h.

Following the indications reported by ISO 1567:1999, a special device, called the "Flexural Test Rig" (FTR), was projected and developed (Fig. 2). The FTR was milled from an aluminum alloy bar; bit and cylindrical supports were made in stainless steel. This appliance allows the specimen to be properly positioned on the test machine (Triaxial Tester T400 Digital, Controls, *Milan, MI, Italy*) so that the test can be carried out in water. Flexural strength was measured with a 3-point bending test. The load was applied at a crosshead speed of 5 mm/min until specimen failure. The load at failure was measured in Newtons (N).

According to ISO 1567:1999, the flexural strength, σ , in MegaPascals (MPa), was calculated from the following equation: $\sigma = \frac{3Fl}{2bh^2}$ where

- F is the maximum load (load at failure), in N;
- l is the distance between the supports, in mm;
- b is the width of the specimen measured immediately prior to water storage, in mm;
- h is the height of the specimen measured immediately prior to

water storage, in mm.

As the same FTR was used for every test, l had a constant value of 50 mm. F (fracture load) ranged from 87,46 to 147,45 N.

The Kolmogorov-Smirnov test and the Levene test were applied to verify the normality of data distribution and the variance homogeneity respectively. The One-Way ANOVA was then applied, followed by the Tukey test for post-hoc comparisons. In all the analyses the significance level was established at $p = 0.05$.

The statistically analyses were performed with SPSS v.12.0.

Results

Table 3 reports mean and standard deviation values of the flexural strengths measured for each group.

The following results were obtained:

- The polymerization cycle has no or minimal influence on the flexural strength of the tested resins;
- The flexural strength of the tested resins were not significantly improved when the slow polymerization cycle were used;
- Group 6 measured higher flexural strength than groups 3, 5, 7 and 9;
- Group 8 measured the lowest flexural strength;
- Groups 3, 7 and 8 measured lower flexural strength compared with other resins;

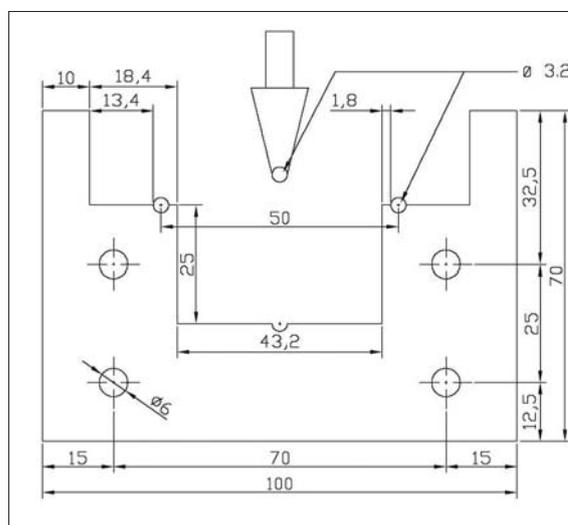


Fig. 2 - FTR project. Frontal view, central section. Measurements in mm.

Table. 3 - Mean values of flexural strength and Standard Deviations of the experimental groups.

Groups with the same superscript letters are not statistically different.

Group	N	Mean and SD
1	6	82,320 ± 5,737 ^{b,c,d,e}
2	6	84,993 ± 5,308 ^{b,c,d,e}
3	6	77,237 ± 5,535 ^{a,b}
4	6	88,306 ± 3,300 ^{d,e}
5	6	80,271 ± 3,252 ^{b,c,d}
6	6	89,273 ± 3,335 ^e
7	6	78,467 ± 5,623 ^{a,b,c}
8	6	71,198 ± 3,775 ^a
9	6	81,007 ± 3,018 ^{b,c,d}
10	6	81,742 ± 3,372 ^{b,c,d,e}
11	6	86,321 ± 2,653 ^{c,d,e}
Total	66	81,922 ± 6,380

Among the polymerization cycles possible with PBH, Group 4 produced specimens with significantly higher flexural strength than Groups 3 and 5. The latter first yielded the specimens with the lowest flexural strength of the PBH subgroup.

Statistically significant differences ($p < 0.05$) were found between the following groups: 4 vs 3 and 5; 6 vs 3, 5, 7, 8 and 9; 8 vs 1, 2; 4, 5, 6, 9, 10, 11.

Discussion

The resins used in this study showed different flexural strength values when the resin type was changed. The first null hypothesis should therefore be rejected.

The results obtained by CLT appear more relevant when related to the presence of aesthetic fibres. As described by Vallittu, a good impregnation of the fibers with the resin is difficult to achieve^{15,29}. This effect is more evident in heat-polymerized resin, which forms a high viscous dough stage with poor wetting properties³⁰. The bonding of the fibers to the resin matrix is a prerequisite for the strength of fiber-reinforced material³¹. Whilst aesthetic fibers are not mixed with the aim of reinforcing the resin, a fiber with an untreated surface does not bond with the resin matrix. This causes the formation of voids, decreasing the mechanical properties of the resin³². Furthermore, an oxygen reserve remains in voids between fibers and the resin matrix, which can inhibit the radical polymerization of the resin, increasing the residual monomer content in the fiber zone and reducing the strength of the material³³. For these reasons, the lack of structural continuity integration between fibers and resin could

negatively affect the resistance of the material and may explain the low flexural strength indicated by CLT, which contains a high amount of thick fibers.

The mechanical properties of the materials in relation to their chemical composition was not analyzed in this study. Most of the heat-polymerizable polymers provided in powder and liquid form, classified by ISO in Type 1 Class 1², present similar compositions³⁴⁻⁴⁴: the powder contains polymethylmethacrylate in approximately 95%, benzoyl peroxyde as initiator (1%) and other additives in the remaining 4% (plasticizer, opacifier and coloring substances); the liquid contains methylmethacrylate and dimethacrylate as cross-linking agents in variable ratios, often around 90:10, and other substances in a small percentage (hydroquinone as a reaction inhibitor and others). Various Authors have demonstrated the importance of the cross-linking agent on the mechanical properties of the denture base materials^{34,38,41,42}, showing that different chemical composition may result in different mechanical performances.

In the case of polymerization cycles, only one statistically significant result was found (group 3 vs 4). The second null hypothesis should therefore be accepted.

From the results obtained, a fast polymerization cycle improved the flexural strength of group 4, in which both the initial and final temperatures were 100°C. Due to the well-known concept that during the exothermic reaction of polymerization, the released heat has to be added to that generated externally, raising the resin temperature⁴⁵, several Authors hypothesized that, in fast polymerization cycles, the total heat could exceed the boiling point of the monomer, causing internal porosity that could affect the mechanical properties of the material⁴⁶⁻⁴⁸. This was demonstrated to be incorrect by Yau et al.⁴⁹, who showed that that in clamped denture flasks immersed in water at 100°C, the boiling point of the monomer was raised to 228°C at 22 atm pressure, whereas the maximum observed temperature of the resin was 131°C. For this reason, fast polymerization cycles will not cause internal porosity if the flasks are maintained under sufficient pressure.

Specimens polymerized with a start-temperature of almost 70°C measured a lower flexural strength compared with others, as showed by Group 3 (70°C), Group 7 and Group 8 (73°C), which produced the worst results. In all the other experimental groups the polymerization cycles started at ambient temperature (23°C), with the exception of Group 4, which started at 100°C.

Further studies would be advantageous in investigating possible physical and/or chemical explanations of the findings of the present study.

Conclusion

All the obtained data must be interpreted exclusively as indicative of the flexural strength of the materials tested. The measure of flexural strength was used only as a reference parameter to compare different material and different polymerization cycles, but not to establish the absolute resistance of the materials to the masticatory loads.

Within the limitations of this study, the following conclusions could be formulated:

- Flexural strength is correlated to the resin type
- The polymerization cycle has no or minimal influence on the flexural strength of the tested resins
- With regard to flexural strength, slow polymerization cycles did not show any significant advantages for all they tested resins
- CLT demonstrated the lowest mean flexural strength value
- The fast polymerization cycle proved to increase the flexural strength of PBH, although the manufacturer recommends the use of this cycle only if the thickness of the prosthesis thickness is ≥ 3 mm.

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