

Physical properties of experimental light-curing pattern resins based on poly(n-butyl methacrylate) or poly(iso-butyl methacrylate)

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Experimental light-curing pattern resins were fabricated to produce pattern resin materials with adequate dimensional stability. The light-curing pattern resins consisted of poly(n-butyl methacrylate) or poly(iso-butyl methacrylate) (PiBMA) polymers and methacrylate monomers. The physical properties, amount of residual ash after burning, Vickers hardness, flexural strength, and volumetric polymerization shrinkage of each material were determined. The data obtained for the prepared resins were compared with those of a commercially available pattern resin, Palavit G (PG). A lower amount of residual ash was observed for some of the prepared resins than for PG. The Vickers hardness and flexural strength values of all experimental resins were lower than those of PG. The volumetric polymerization shrinkage of all the experimental resins based on PiBMA was lower than that of PG. These results suggest that acrylic light-curing resin materials based on PiBMA may be useful for patterning and indexing during soldering.

Keywords: Pattern resin, Residual ash, Vickers hardness, Flexural strength, Polymerization shrinkage

INTRODUCTION

Acrylic pattern resin materials have been widely used in dentistry for many purposes since their introduction¹. They have been recommended for direct post and core patterns^{2,3}, intraoral soldering indices for multiple-unit fixed partial dentures^{4,6}, metal frames or clasp patterns of removable partial dentures⁷, fabrication of new crowns to fit existing removable partial dentures^{8,9} and outer caps of cone telescopic crowns¹⁰. Recently, pattern resins have been used for implant prosthesis fabrication. Fitting implant restoration passively without undue stress is required to avoid complications such as alveolar bone resorption, abutment fracture, and connecting screw breakage¹¹. These requirements can be achieved by accurately transferring the intraoral implant positions to working casts¹²⁻¹⁵. Impression copings and laboratory analogs must be splinted rigidly without positional displacement using pattern resins through the impression procedures. These pattern resin materials have several advantages over waxes, impression compounds, and plaster materials, including low coefficients of thermal expansion, low tendency for stress relaxation, and high mechanical strength¹⁶. The flexural strength of commercially available pattern resins [Palavit G (PG; Kulzer, Hamburg, Germany) and GC pattern resin (GC, Tokyo, Japan)] was reported as 112.8 MPa and 74.5 MPa respectively¹⁷. Yamahachi, a dental manufacturer, provided information about the self-curing pattern resin Pattern Bright (Yamahachi Dental, Gamagori, Japan). According to the information provided, the Vickers hardness value and flexural strength of the resin were 13.4 and 60 MPa, respectively.

Pattern resins are expected to be useful in clinical dentistry. However, inadequate dimensional stability caused by polymerization shrinkage has been reported for various applications of acrylic resins, especially those involving patterns and indices. Because most of these pattern resins are based on methyl methacrylate (MMA), shrinkage occurs during polymerization. However, almost no reports have been published on improving the properties of pattern resins. Pattern resin materials must leave little residual ash after burning. Therefore, we attempted to produce new acrylic pattern resins with a low amount of residual ash after burning and adequate dimensional stability. In addition, we produced a light-polymerization type resin, which is easier to operate than a self-polymerization type. In this study, we selected poly(n-butyl methacrylate) (PnBMA) or poly(iso-butyl methacrylate) (PiBMA) polymers, which leave low amounts of ash after burning, as advertised by their manufacturers. Because it is unclear which monomers are effective for mixing, we selected several monomers for use as dental materials: MMA, ethyl methacrylate (EMA), butyl methacrylate (BMA), and ethylene glycol dimethacrylate (EGDMA). The residual ash after burning, Vickers hardness, flexural strength, and volumetric polymerization shrinkage of each material were evaluated. The data obtained for the prepared resins were compared with those of a commercially available pattern resin, PG.

MATERIALS AND METHODS

Materials

Acrylic light-curing resin materials were produced



using PnBMA or PiBMA polymers and monomers such as MMA, EMA, BMA, and EGDMA. To light-cure the materials, camphorquinone (Wako Pure Chemical, Osaka, Japan) as a photosensitizer and N-N dimethylamino ethylmethacrylate (Wako Pure Chemical) as a reducing agent were dissolved in the monomer to a final concentration of 1 wt%. Palavit G, a commercially available self-curing pattern resin, was selected as the control material. The materials used in this study are listed in Table 1.

Specimen preparation

The powder-to-liquid (P/L; g/mL) ratios varied from 0.9 to 1.4 for pattern resin materials based on PnBMA and from 1.9 to 2.7 for those based on PiBMA. The powder-to-liquid ratio for each combination was determined in a preliminary trial considering clinically manageable consistency in order to fabricate specimens whose deformability was similar to that of a traditional pattern resin material^{18,19}. However, the wettability between PnBMA polymer and EGDMA monomer was exceedingly poor, making it difficult to fabricate the specimen from these two materials. Therefore, this combination was excluded from the study. For PG, the P/L ratio was set to

2.0, as described by Morikawa *et al.*²⁰ and Nakashima²¹. The compositions of the resins used in this study are listed in Table 2. For residual ash, Vickers hardness, and polymerization shrinkage, the powder and liquid were hand spatulated for 40 s and packed into a cylindrical metal mold divided into two pieces. The mold had an internal diameter of 6 mm and length of 10 mm. Petroleum jelly was lightly applied to the mold to prevent the mixture from bonding. The mold was overfilled with the mixture and placed between flat glass plates. The excess mixture was removed using hand pressure and a cutter knife. The specimens were removed from the mold in the dough stage. Subsequently, each specimen except PG was irradiated using a visible light source (α -Light, Morita, Tokyo, Japan) for 5 min.

For flexural strength, the powder and liquid were hand spatulated for 40 s and packed into a Teflon mold with width, depth, and length of 3, 2, and 35 mm, respectively²². The top surface of the Teflon mold was covered with a flat glass plate. Each specimen except PG was irradiated using a visible light source for 5 min (α -Light).

Table 1 Materials used in this study

Material	Product	Manufacturer	Code
Methacrylate polymer			
Poly(n-butyl methacrylate)	M-6003	Negami Chemical, Nomi, Japan	PnBMA
Poly(iso-butyl methacrylate)	M-0605	Negami Chemical	PiBMA
Methacrylate monomer			
Methyl methacrylate	—	Wako Pure Chemical, Osaka, Japan	MMA
Ethyl methacrylate	—	Wako Pure Chemical	EMA
Butyl methacrylate	—	Wako Pure Chemical	BMA
Ethylene glycol dimethacrylate	—	Wako Pure Chemical	EGDMA
Pattern resin	Palavit G	Kulzer, Hamburg, Germany	PG

Table 2 Compositions of pattern resin materials used in this study

Polymer	Monomer	P/L ratio (g/mL)	Code
PnBMA	MMA	0.9/1	nM
PnBMA	EMA	1.2/1	nE
PnBMA	BMA	1.4/1	nB
PiBMA	MMA	1.9/1	iM
PiBMA	EMA	2.4/1	iE
PiBMA	BMA	2.7/1	iB
PiBMA	EGDMA	2.5/1	iED
PMMA	MMA	2.0/1	PG (Palavit G)

The amount of residual ash after burning

Twenty-four specimens of each resin material were prepared and divided into eight groups of three specimens. The three specimens of each group were stored in a desiccator for one week after polymerization and weighed using an electronic balance with an accuracy of 0.01 mg (ER-182A, A&D, Tokyo, Japan) at constant temperature ($23\pm 0.5^\circ\text{C}$). The specimens were then burned in a porcelain crucible placed inside a furnace at 700°C for 2 h. The residual ash of each specimen after burning was weighed at the same constant temperature ($23\pm 0.5^\circ\text{C}$) and expressed as a proportion of the initial weight before burning. This experiment was performed for all eight groups.

Vickers hardness

The bottom surfaces of the cylindrical specimens were polished using a series of silicon carbide abrasive disks (P#300, P#600, and P#1200; Sankyo Rikagaku, Tokyo, Japan). After 24 h of polymerization, Vickers hardness tests were performed with eight specimens of each resin material using a microhardness tester (MVK-E, Akashi, Yokohama, Japan) under a 50 g load for 30 s.

Flexural strength

The top and bottom surfaces of the rectangular specimens were polished in the same manner as described above. After 24 h of polymerization, three-point flexural strength tests were performed with eight specimens of each resin material using a universal testing machine (TGE-5kN, Minebea, Nagano, Japan) at a crosshead speed of 0.5 mm/min. The distance between the two support points was 15.0 mm.

Polymerization shrinkage

The change in the density of each specimen before and after polymerization was measured using a pycnometer (TGM, Tokyo, Japan) filled with 5 mL distilled water. The specimens were immersed in an ethyl alcohol solution (Ethanol, 99.5%, Wako Pure Chemical) for a few seconds to prevent air bubbles from attaching to their surface. The density of each specimen (D) was calculated as follows:

$$D = \frac{W_s \cdot S}{W_s - (W_a - W_b)}$$

where W_s is weight of the specimen, S is density of the distilled water at 23°C , W_a is weight of the pycnometer filled with distilled water and specimen, and W_b is weight of the pycnometer filled with distilled water only. The temperature around the sample was kept constant at $23\pm 0.5^\circ\text{C}$. The change in the density of each specimen before and after polymerization was converted into a volumetric change. The percentage volumetric polymerization shrinkage (σ) was expressed as a proportion of the initial volume before polymerization. This equation can be written as

$$\sigma = \frac{V_b - V_a}{V_b} \times 100 = \frac{M/D_b - M/D_a}{M/D_b} \times 100 = \left(1 - \frac{D_b}{D_a}\right) \times 100$$

where V_a is volume of the specimen after polymerization, V_b is volume of the specimen before polymerization, M is weight of the specimen, D_a is density of the specimen after polymerization, and D_b is density of the specimen before polymerization. The measurements before polymerization were performed prior to light irradiation for the experimental resin materials and immediately after mixing for PG. The measurement after polymerization was performed 20 min after light irradiation of the experimental resin materials and 20 min after the beginning of mixing for PG. Eight specimens for each resin material were used to study polymerization shrinkage.

Scanning electron microscopy observation

The three polymers used in this study for pattern resin materials were sputter-coated with a thin layer of Au-Pd under vacuum using ion sputter (JFC-1100E, JOEL, Tokyo, Japan) and observed by scanning electron microscopy (SEM; JSM-35CF, JEOL) at an operating voltage of 15 kV. Images were captured at a $200\times$ magnification. The particle sizes and shapes of the three polymers were examined.

Statistical analysis

A one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison test were performed to analyze significant differences in the data; a significance level of 0.05 was observed. These analyses were performed using a statistical software (BellCurve, SSRI, Tokyo, Japan).

RESULTS

Figure 1 shows the residual ash content of each resin after burning. The amount of residual ash of all the experimental resin materials did not increase compared to that of PG, and the decrease was statistically significant for nB and iB ($p < 0.05$).

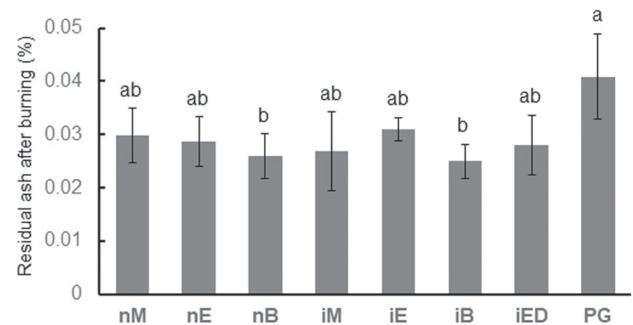


Fig. 1 Residual ash of each resin material after burning. Same letters indicate no significant differences ($p > 0.05$).

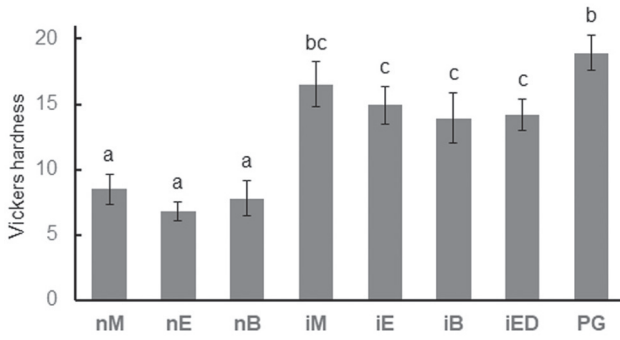


Fig. 2 Vickers hardness of each resin material after polymerization. Same letters indicate no significant differences ($p>0.05$).

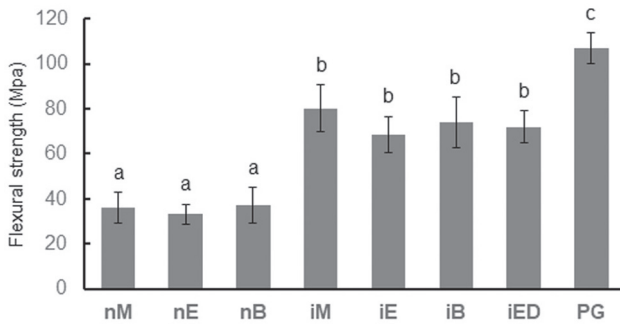


Fig. 3 Flexural strength of each resin material after polymerization. Same letters indicate no significant differences ($p>0.05$).

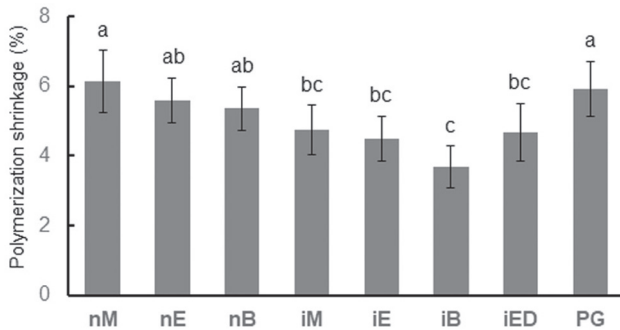


Fig. 4 Volumetric polymerization shrinkage of each resin material. Same letters indicate no significant differences ($p>0.05$).

Figure 2 shows the Vickers hardness values of each resin material after polymerization. Most of the experimental resins were significantly less hard than PG ($p<0.05$). However, no significant difference in hardness value was observed between iM and PG ($p>0.05$).

Figure 3 shows the flexural strength of each resin

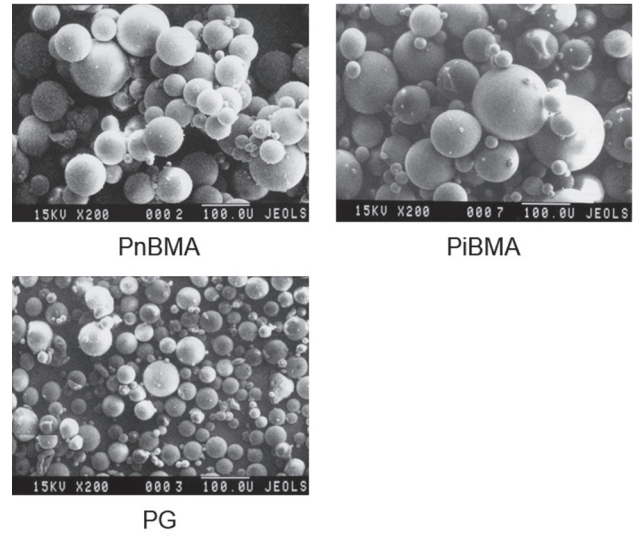


Fig. 5 SEM pictures of three polymers used in this study.

after polymerization. The flexural strength of each experimental resin material was significantly lower than that of PG ($p<0.05$).

Figure 4 shows the volumetric polymerization shrinkage of each resin material, converted from the variation in density before and after polymerization. No significant difference in polymerization shrinkage was observed between the PnBMA-based resins and PG. However, compared with PG, all the experimental PiBMA-based resins underwent less polymerization shrinkage. The polymerization shrinkage of PiBMA-based resins was 20%–38% lower than that of PG. In particular, the value of iB was the lowest among all materials examined.

The SEM images of the three polymers used in this study are shown in Fig. 5. The three polymer particles have a similar spherical shape. The polymer particle sizes differed considerably. The particle size of PiBMA was close to 100 μm , which was larger than that of other two polymers.

DISCUSSION

Pattern resin materials should have physical properties such as a small amount of residual ash after burning and some degree of mechanical strength to prevent deformation or fracture when they are placed or removed during prosthetic procedures, and low polymerization shrinkage to produce accurate prostheses.

According to the information provided by the manufacturer, the PnBMA and PiBMA leave a low amount of residual ash after burning. Therefore, these two polymers were selected for this study. None of the experimental resin materials yielded more residual ash than PG after burning (Fig. 1). The nB and iB specimens yielded significantly less residual ash than PG. Because the experimental resin materials did not contain

pigments, the amount of residual ash they yielded was slightly less than that yielded by PG. However, according to the information provided by the manufacturer, the influence of the pigment on the residual ash appeared to be negligible. Yamahachi, a dental manufacturer, provided information about the self-curing pattern resin (Pattern Bright). According to the information provided, the residual ash content of Pattern Bright at 700°C was 0.067%. Therefore, all the experimental resin materials can be used from the viewpoint of residual ash.

The hardness values of almost all the experimental resins were lower than those of PG (18.92) (Fig. 2). There was no statistically significant difference in hardness values between iM and PG. The hardness of PiBMA-based resins ranged from 13.94 to 16.52. A possible explanation for this is the difference in their molecular weights. According to the information provided by the manufacturer, the molecular weights of PnBMA (290,000) and PiBMA (260,000) are lower than that of polymethyl methacrylate (330,000–350,000). Therefore, almost all the experimental resin materials were less hard than PG. The flexural strength of each experimental resin material was significantly lower than that of PG (Fig. 3). The flexural strength of PiBMA-based resins were in the range of 68.4–80.2 MPa. The mechanical strength of the experimental resins based on PiBMA is presumed to be equivalent to that of GC pattern resin (74.5 MPa)¹⁷ or Pattern Bright (60 MPa). Danesh *et al.* reported that resin materials based on iso-/n-butyl methacrylate could be used as occlusal splints to withstand masticatory pressure²³. Experimental resins based on PiBMA may be considered to have acceptable mechanical strengths for pattern and index materials.

Several methods have been used to determine the dimensional accuracy and polymerization shrinkage of acrylic pattern resins. Kusakai measured the linear polymerization shrinkage of three self-curing pattern resins [GC pattern resin, PG, and Duralay (Reliance Dental, Worth, Ill, USA)] poured into a metal mold²⁴. The linear shrinkage values ranged from 0.67% to 0.83%. He reported that the shrinkage values were smaller than predicted because of the existence of residual monomers and the contact of the specimens with the metal mold. Harper and Nicholls measured the distortion in several indexing materials and found that zinc oxide and eugenol paste produced substantially less mean distortion than other indexing materials such as pattern resin⁵. Although citing that literature, Katoh reported that the use of pattern resin is popular in clinical practice because of its easy manipulation⁶. Nakashima reported that the main component of PG is MMA, which was measured using liquid chromatography²¹. The theoretical polymerization shrinkage of pure MMA was reported to be approximately 21% by Mojon *et al.*¹⁸. The P/L ratio of PG was 2.0; therefore, the total polymerization shrinkage was approximately 7%. Although PG is based on MMA, the polymerization shrinkage of 5.93% (Fig. 4) observed in this study was slightly lower than the predicted value of 7%. This was probably due to the influence of residual monomers and other substances present in PG,

which were not disclosed by the manufacturer. However, this value is similar to the results of several previous studies on the dimensional accuracy of pattern resins. Mojon *et al.* measured the volumetric polymerization shrinkage of two self-curing resins (Duralay and PG) using a dilatometer and linear inductive transducer¹⁸. They found that the mean volumetric shrinkage reached 6.5% for Duralay and 5.5% for PG 17 min after the start of mixing. They suggested that these resins are not dimensionally stable and should be used with a method that compensates for their shrinkage when they are employed as an index material. Gibbs *et al.* reported the volumetric polymerization shrinkage of two self-curing pattern resins (Duralay and GC pattern resin) and two light-curing pattern resins [Primopattern LC Gel (Primotec, Norwalk, CT, USA) and Primopattern LC Paste (Primotec)]¹⁹. The polymerization shrinkage was determined by measuring the changes in the area of the specimens using image analysis. The volumetric shrinkage values were 5.07, 5.72, 5.42, and 7.43% for the Duralay, GC pattern resin, Primopattern LC Gel, and Primopattern LC Paste, respectively. The volumetric shrinkage of the Primopattern LC Paste was significantly higher than those of the other three materials. They reported that a higher polymerization shrinkage might affect the accuracy of implant prosthesis fabrication. Danesh *et al.* used a hydrostatic method to evaluate the volumetric polymerization shrinkage of self-curing resins based on MMA (Palapress, Kulzer) and light-curing resins based on iso-/n-butyl methacrylate (Acrylight, Schütz Dental, Rosbach, Germany) for occlusal splints²³. They reported a value of 6.1% for Palapress and 6.2% for Acrylight. No statistically significant differences were observed between the two materials.

In this study, volumetric polymerization shrinkage was calculated from the change in density of each material before and after polymerization using a pycnometer (buoyancy method). This method does not require dedicated shrinkage measuring equipment. Conventional pycnometer shrinkage measurement techniques provide a “free” shrinkage value, which means that the specimens shrink without any hindrance from the surrounding media¹⁹. As shown in Fig. 4, a small difference was observed between PnBMA-based resins and PG in terms of polymerization shrinkage. However, all PiBMA-based resins underwent less polymerization shrinkage than PG. In particular, the combination of PiBMA and BMA resulted in a minimal volumetric polymerization shrinkage (3.70%). As expected, the combination specimen with a thick P/L ratio exhibited less volumetric polymerization shrinkage. Although the experimental resins based on PnBMA with thin P/L ratios were expected to show large polymerization shrinkage, measurements were carried out to comprehensively evaluate the physical properties required for the pattern resin. As shown in Fig. 5, the three polymer particles have a similar spherical shape. The polymer particle sizes differed considerably. The particle size of PiBMA was approximately 100 µm, which is larger than that of other polymers. In addition, the particle size distribution

of PnBMA appeared to be considerably dispersed. The wettability between PiBMA polymer particles and each monomer may be good because of their small specific surface areas. Therefore, the powder-to-liquid ratio increased, and a low volumetric polymerization shrinkage was observed in the PiBMA-based resins. This property is clinically favorable for accurate prosthetic applications.

For future clinical applications, the thermal expansion behavior and effects on the dental casting investment of experimental pattern resins during burning in a furnace should be investigated²⁵. In summary, new experimental acrylic light-curing pattern resin materials based on PnBMA or PiBMA were introduced to overcome the disadvantages of conventional self-curing pattern and index resins based on MMA. Several polymerization characteristics were evaluated. Within the limitations of this study, the experimental resins based on PiBMA, especially those that combined PiBMA and BMA, appeared to be suitable as pattern and index materials. These materials left a low amount of residual ash after burning and exhibited acceptable mechanical strength. Furthermore, they exhibited adequate dimensional stability owing to their low polymerization shrinkage.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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