

THE EFFECT OF MONOMER TO POWDER RATIO ON POLYMERIZATION SHRINKAGE-STRAIN KINETICS OF POLYMER-BASED PROVISIONAL CROWN AND FIXED PARTIAL DENTURE MATERIALS

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Statement of problem. Although a number of previous investigations have been carried out on the polymerization shrinkage-strain kinetics of provisional crown and fixed partial denture (FPD) materials, the effect of the changes of liquid monomer to powder ratio on its polymerization shrinkage-strain kinetics has not been reported.

Purpose. The purpose of this study was to investigate the influence of liquid monomer to powder ratio of polymer-based provisional crown and FPD materials on the polymerization shrinkage-strain kinetics.

Material and methods. Chemically activated acrylic provisional materials (Alike, Jet, Snap) were investigated. Each material was mixed with different liquid monomer to powder ratios by volume (1.0:3.0, 1.0:2.5, 1.0:2.0, 1.0:1.5, 1.0:1.0). Time dependent polymerization shrinkage-strain kinetics of all materials was measured by the bonded-disk method as a function of time at 23 °C. Five recordings were taken for each ratio. The results were statistically analyzed using one-way ANOVA and the multiple comparison Scheffe test at the significance level of 0.05. Trends were also examined by linear regression.

Results. At 5 minutes after mixing, the polymerization shrinkage-strains of all materials ranged from only 0.01% to 0.49 %. At 10 minutes, the shrinkage-strain of Alike was the highest, 3.45 % (liquid monomer to powder ratio = 1.0:3.0). Jet and Snap were 2.69 % (1.0:2.0) and 1.58 % (1.0:3.0), respectively ($P > 0.05$). Most shrinkage (94.3 % - 96.5 %) occurred at 30 minutes after mixing for liquid monomer to powder ratio, ranging from 1.0:3.0 to 1.0:1.0. The highest polymerization shrinkage-strain values were observed for the liquid monomer to powder ratio of 1.0:3.0. At 120 minutes after mixing, the shrinkage-strain values were 4.67 %, 4.18 %, and 3.07 % for Jet, Alike, and Snap, respectively. As the liquid monomer to powder ratio increased, the shrinkage-strain values tend to be decreased linearly ($r = -0.769$ for Alike, -0.717 for Jet, -0.435 for Snap, $r^2 = 0.592$ for Alike, 0.515 for Jet, 0.189 for Snap; $P < 0.05$).

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Conclusion. The increase of the liquid monomer to powder ratio from 1.0:3.0 to 1.0:1.0 had a significant effect on the shrinkage-strain kinetics of polymer-based crown and FPD materials investigated. This increased the working time and decreased the shrinkage-strain during polymerization.

Key Words

Polymerization shrinkage-strain kinetics, Monomer to powder ratio, the Bonded-disk method, Provisional crown and fixed partial denture material

Provisional restorations are an integral part of dental therapy.¹ They can be used as a guide for definitive prosthetic treatment. Many materials can be used as a provisional prosthesis, but the most widely used materials for a provisional prosthesis are tooth-colored, polymer-based materials, such as polymethyl methacrylate, higher (meth) acrylate and dimethacrylate. They are the materials of choice when esthetics is of primary concern. Among them, monomethacrylate-based provisional crown and fixed partial denture (FPD) materials have been widely used in dentistry because they are cheap and can be easily added on.² One of the inherent properties of monomethacrylate-based provisional crown and FPD materials is a dimensional change during polymerization. Monomers are converted into their corresponding polymeric form during free radical polymerization processes, which results in a density change as the liquid monomer, typically lower density, converts to a polymer of higher density. It is this density change that is the primary source of shrinkage.³ This is known as polymerization shrinkage, which may cause several clinical problems. The shrinkage may cause distortion that may jeopardize the accurate fit to the prepared teeth and also internal stress within the restorations, leading to poorly fitting prostheses.^{2,4,5,6} Poor marginal fit allows passage of oral fluids and bacteria into the gap, and also allows the deposition of bacterial plaque. This can

contribute to localized periodontal inflammation. As a consequence, the periodontal health and the integrity of the prepared tooth structure may be damaged.⁷⁻¹³ Hence, it is crucial to know that the polymerization shrinkage kinetics and the amount of shrinkage-strain of the polymer-based crown and FPD materials before using them to reduce the above clinical complications. Monomethacrylate-based provisional crown and FPD materials are presented as a liquid and a powder that can be mixed in room temperature. In many clinical cases, dentists tend to change the liquid monomer to powder ratio in the fabrication of polymer-based provisional crown and FPDs. Although a number of previous investigations have been carried out on the polymerization shrinkage-strain kinetics of provisional crown and FPD materials, the effect of the changes of liquid monomer to powder ratio on its polymerization shrinkage-strain kinetics has not been reported. Thus, the purposes of this study were (i) to measure the polymerization shrinkage kinetics and strain of three polymer-based provisional crown and FPD materials and (ii) to investigate the effect of liquid monomer to powder ratio on the polymerization shrinkage kinetics and strain of the materials investigated. The null hypothesis to be tested was that there was no difference in the polymerization shrinkage-strain of polymer-based provisional crown and FPD materials with different liquid monomer to powder ratio.

MATERIAL AND METHODS

The materials used in this study are monomethacrylate-based materials, and presented in Table I. All materials are chemically activated resins, and a powder and liquid system. They were mixed and initiated in accordance with manufacturers' instructions. The powder component was added to the liquid in a polymeric bowl. Then these components were stirred with a plastic spatula. Each material took a period of time, circa 20 seconds to mix with different liquid monomer to powder ratios by volume (1.0:3.0, 1.0:2.5, 1.0:2.0, 1.0:1.5, 1.0:1.0). Each component was mixed manually until the powder was completely wetted by the monomer.

Time dependent polymerization shrinkage-strain kinetics of all materials was measured by 'Watts' method.¹⁴ The device consisted of an aluminum stand and a horizontal table that was capable of clamping a Linear Variable Displacement Transformer (LVDT, GT 2000, RDP Electronics Ltd, Wolverhampton, UK). A brass anvil 40 mm in diameter was positioned beneath the horizontal table. Each mixed specimen was placed centrally within the center of the brass ring of 1 mm thickness and 16 mm internal diameter fixed on a glass plate (Fig. 1). A flexible, thin, compliant (25 mm × 25 mm × 0.1 mm) microscope glass cover-slip (Type 0, Chance-Propper Ltd, Warley, UK) was placed over the upper specimen and was supported on a brass ring. The cover-slip was flattened to ensure that it was in contact with the supporting ring and the specimen evenly. As such, each specimen was shaped with the

same dimensions of 1 mm in thickness and *circa* 8 mm in diameter (50 mm³). The cover-slip was deflected as the specimen shrank during polymerization. Its deflection at the center of the cover-slip was measured continuously by a precision linear variable displacement transducer (LVDT, type GT 2000, RDP Electronics, Wolverhampton, UK) with a sensitivity of over 0.1 μm which was positioned vertically onto the center of the cover-slip. The axial dimensional change was monitored over time, up to 120 min after the completion of the mixing in units of voltage by the LVDT. The data was transferred to a signal conditioning unit (Type E307-3, RDP Electronics, Wolverhampton, UK), and then to a Picolog software (Version 5.03.2, Pico Technology Ltd, St Neots, Cambridgeshire, UK). The displacement of the cover-slip (the amount of linear contraction: $\Delta L = L_0 - L$; where L_0 is the original specimen thickness and L is the final thickness) was determined with Fig.P software (The Scientific Fig.

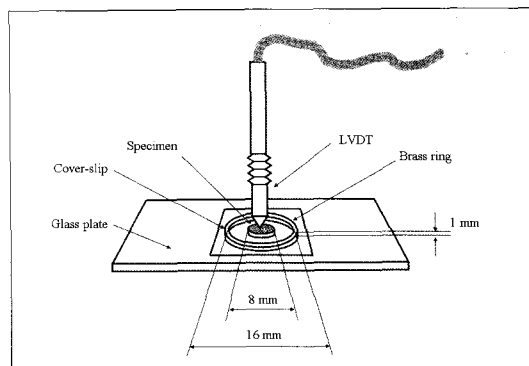


Fig. 1. Bonded-disk measurement apparatus used in this study.

Table I. The polymer-based provisional materials investigated

Material	Characteristics	Lot No.	Shade	Manufacturer
Alike	Monomethacrylates	401051	67/B3	COE, Alsip, Ill, USA
Snap	Monomethacrylates	90306	65/D3	Parkell, Farmingdale, NY, USA
Jet	Monomethacrylates	14302040	66/A3	Lang Dental Mfg. Co. Inc, Chicago, Ill, USA.

Processor, Version 2.98, Fig.P Software Corporation, Durham, NC, USA) via the calibration coefficient of displacement/voltage (3.4×10^6 mm/mV). This displacement (ΔL) was divided by L_0 and multiplied by 100 to get a percentage of shrinkage-strain as a function of time. All experiments were carried out in five times at 23 ± 0.5 °C.

The results were statistically analyzed using one-way ANOVA and the multiple comparison Scheffe test at the significance level of 0.05. Trends were also examined by linear regression. SPSS software (Version 12.0, SPSS Inc., Chicago, Ill, USA) was used for these statistical analyses.

RESULTS

The polymerization shrinkage kinetic curves of each material are presented in Fig. 2-4. The results of the polymerization shrinkage-strain are given in Table II. The results showed an increase of polymerization shrinkage-strain in magnitude up to 120 minutes after the start of mixing.

At 5 minutes after mixing, the polymerization shrinkage-strains of all materials ranged from only 0.01% to 0.49 %. This was caused by the

slow onset of setting. At 10 minutes, the shrinkage-strain of Alike was the highest, 3.45 % (liquid monomer to powder ratio = 1.0:3.0). Jet and Snap were 2.69 % (1.0:2.0) and 1.58 % (1.0:3.0) respectively. The values between Jet and Snap were not significantly different ($P > 0.05$). Most shrinkage (94.3 % - 96.5 %) occurred at 30 minutes after mixing for liquid monomer to powder ratio, ranging from 1.0:3.0 to 1.0:1.0 except Snap (1:1.5), but the shrinkage continued up to 120 minutes after the start of mixing. The highest polymerization shrinkage-strain values were observed for the liquid monomer to powder ratio of 1.0:3.0. At 120 minutes after mixing, the shrinkage-strain values were 4.67 %, 4.18 %, and 3.07 % for Jet, Alike, and Snap, respectively. Both Jet and Alike showed similar shrinkage values ($P = 0.049$). The value of Snap was significantly different from that of Alike or Jet ($P < 0.05$).

As the liquid monomer to powder ratio increased, the shrinkage-strain values tend to be decreased linearly (Fig. 5) ($r = -0.769$ for Alike, -0.717 for Jet, -0.435 for Snap, $r^2 = 0.592$ for Alike, 0.515 for Jet, 0.189 for Snap; $P < 0.05$). The shrinkage-strain values for the ratio of 1.0:1.0

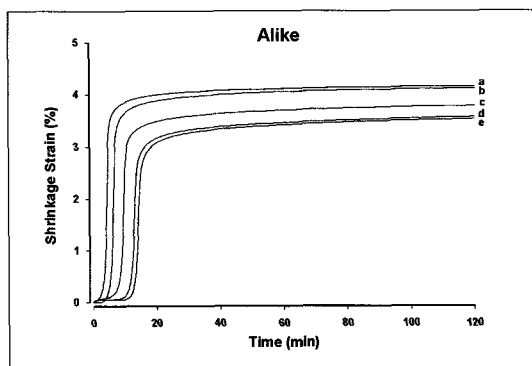


Fig. 2. Polymerization shrinkage-strain kinetic curves of Alike. Each curve is for a different liquid monomer to powder ratio. a) 1.0:3.0, b) 1.0:2.5, c) 1.0:2.0, d) 1.0:1.5, e) 1.0:1.0.

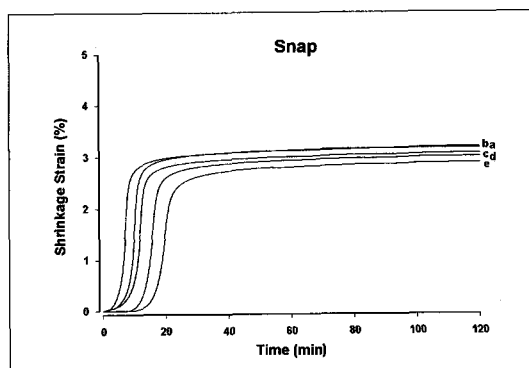


Fig. 3. Polymerization shrinkage-strain kinetic curves of Jet. Each curve is for a different liquid monomer to powder ratio. a) 1.0:3.0, b) 1.0:2.5, c) 1.0:2.0, d) 1.0:1.5, e) 1.0:1.0.

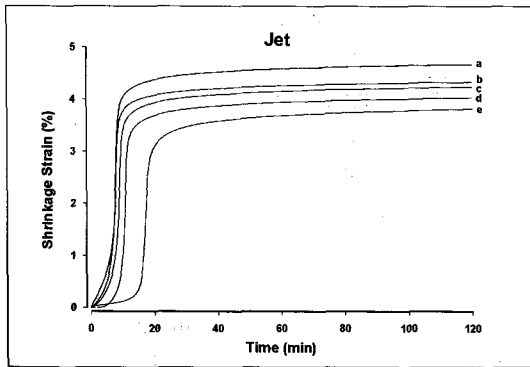


Fig. 4. Polymerization shrinkage-strain kinetic curves of Snap. Each curve is for a different liquid monomer to powder ratio. a) 1.0:3.0, b) 1.0:2.5, c) 1.0:2.0, d) 1.0:1.5, e) 1.0:1.0.

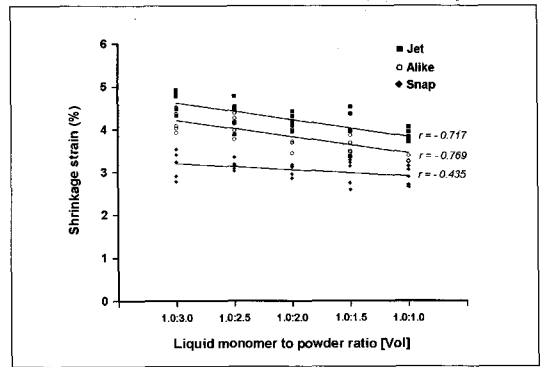


Fig. 5. Linear regression relationship between shrinkage-strain and liquid monomer to powder ratio.

Table II. The mean and standard deviation of the polymerization shrinkage-strain

Material	Liquid monomer to powder ratio	Time at measurement (min)				
		5	10	30	60	120
Alike	1.0:3.0	0.29 (0.08)	3.45 (0.39)	3.94 (0.24)	4.06 (0.26)	4.18 (0.25)
	1.0:2.5	0.24 (0.25)	3.26 (0.30)	3.91 (0.27)	4.04 (0.24)	4.10 (0.24)
	1.0:2.0	0.12 (0.11)	3.19 (0.30)	3.61 (0.25)	3.70 (0.24)	3.77 (0.23)
	1.0:1.5	0.11 (0.10)	0.98 (0.98)	3.39 (0.30)	3.48 (0.18)	3.57 (0.20)
	1.0:1.0	0.02 (0.02)	0.34 (0.36)	3.35 (0.17)	3.45 (0.29)	3.49 (0.28)
	Jet	1.0:3.0	0.49 (0.17)	2.34 (0.93)	4.43 (0.26)	4.58 (0.27)
Jet	1.0:2.5	0.46 (0.11)	2.57 (1.25)	4.16 (0.31)	4.28 (0.34)	4.36 (0.35)
Jet	1.0:2.0	0.36 (0.29)	2.69 (1.32)	4.01 (0.16)	4.11 (0.17)	4.19 (0.18)
Jet	1.0:1.5	0.12 (0.07)	1.10 (0.92)	3.84 (0.40)	3.95 (0.43)	4.03 (0.45)
Jet	1.0:1.0	0.05 (0.05)	0.10 (0.08)	3.39 (0.16)	3.69 (0.14)	3.85 (0.15)
Snap	1.0:3.0	0.21 (0.10)	1.58 (0.77)	2.92 (0.34)	3.08 (0.33)	3.07 (0.32)
	1.0:2.5	0.09 (0.03)	0.66 (0.40)	2.98 (0.13)	3.08 (0.12)	3.15 (0.12)
	1.0:2.0	0.04 (0.05)	0.36 (0.20)	2.92 (0.15)	3.00 (0.15)	3.05 (0.14)
	1.0:1.5	0.02 (0.02)	0.05 (0.05)	2.10 (0.93)	2.88 (0.32)	3.00 (0.31)
	1.0:1.0	0.01 (0.02)	0.03 (0.03)	2.78 (0.20)	2.85 (0.21)	2.88 (0.21)

were significantly lower than those for the ratio of 1.0:3.0 ($P < 0.05$). Jet showed a 17.6 % decrease when the value at the ratio of 1.0:1.0 was compared with that at 1.0:3.0. This was followed by Alike (16.5 %) and Snap (6.2 %). Multiple comparison Scheffe test showed that the increase of the liquid monomer to powder ratio from 1.0:3.0 to 1.0:1.0 had a significant effect ($P < 0.05$) on the shrinkage-strain values of all materials except Snap.

DISCUSSION

Polymer-, especially acrylic-, based provisional crown and FPD material is one of the most widely used biomaterials, being used to serve a guide for definitive prosthetic treatment. Most acrylic-based provisional crown and FPD materials used in the above application are two-part products (liquid monomer and powder system). Chemically they are based on methyl methacrylate, and nearly all of them have the same functional constituents. The constituents of the powder are prepolymerized polymethyl methacrylate beads alone or with a copolymer, and an initiator (usually, benzoyl peroxide) of the polymerization reaction. The liquid monomer constituents are methyl methacrylate, an accelerator/activator/promoter (usually *N,N*-dimethyl-4-toluidine) of the free-radical polymerization reaction, and a stabilizer/inhibitor of that reaction (usually hydroquinone). The shrinkage-strain of liquid methyl methacrylate upon polymerization is circa 21.1%. Such a high polymerization shrinkage-strain can be reduced by the introduction of liquid monomer (methyl methacrylate) and powder (prepolymerized polymethyl methacrylate) system, since only the methyl methacrylate component shrinks during polymerization.

This experiment was conducted with the bonded-disk method for measurement of the shrinkage-strain kinetics. Although there may be a possible source of error for rapid-setting bioma-

terials due to any shrinkage-strain prior to the start of measurement, many studies confirm that the bonded-disk method has determined volumetric shrinkage-strain with the required precision for polymethyl methacrylate/methacrylate self-cure system.^{6,14,15} Most curing of the materials tested regardless of the mixing ratio occurred in the first 30 minutes after mixing. This is in well accordance with the previous study.¹⁶ The results showed the increase of polymerization shrinkage-strain in magnitude continued up to 120 minutes after the start of mixing. It can be expected that an increase of the liquid monomer to powder ratio of the provisional crown and FPD biomaterials significantly increased the final polymerization shrinkage-strain values since the liquid monomer to be reacted in a given volume was increased. But, in fact, according to this result, the polymerization shrinkage-strain values at 120 minutes decreased from 4.67 % to 3.85 % for Jet, from 4.18 % to 3.49 % for Alike, and from 3.07 % to 2.88 % for Snap when the liquid monomer to powder mixing ratio was increased from 1.0:3.0 to 1.0:1.0. For all materials, the correlations were quite linear. Thus, the null hypothesis to be tested could be rejected. This trend noted in the result as a function of mixing ratio was qualitatively similar to the previous study reported for acrylic bone cement.⁶ In dental practice when the polymer-based crown and FPD material is used, utilization of a higher liquid monomer to powder ratio has been frequently occurred because of easy mixing or lack of knowledge for ideal mixing ratio. It is known that the use of higher amounts of liquid monomer increases the working time of the mass and subsequently favors the wetting and swelling of polymethyl methacrylate powder beads by the methyl methacrylate liquid component, and improves handling characteristics of the mixture in the dough state.¹⁷ Thus, it makes fabrication of provisional prosthesis easier. However, altering the recommended liquid monomer to powder

ratio can affect the material behavior of the provisional crown and FPD. There is an explanation for the change in material behavior as a function of liquid monomer to powder ratio. Increasing the liquid monomer content not only increases the liquid monomer to powder ratio and thereby the monomer matrix volume fraction, but effectively decreases the volume fraction of polymethyl methacrylate beads in the monomer matrix. As the monomer matrix volume fraction increases, so too may the volume fraction to react for shrinkage. But, the reason why the increase of the liquid monomer to powder ratio did not increase the polymerization shrinkage is that the increase in liquid monomer to powder ratio likely provides more monomer than can be reacted with the available initiators and thus, unreacted monomer remains in the polymerized materials.¹⁸ This may induce a low level of polymerization and low degree of conversion throughout the provisional prosthesis, which has unwanted residual monomer. This may act as a plasticizer.¹⁹ The increase of liquid monomer to powder ratio of polymer-based provisional prosthesis may induce several clinical problems. Based on this test results, the increase of liquid monomer to powder ratio still leads to the polymerization shrinkage-strain, which may increase the marginal discrepancy of polymer-based provisional prosthesis. There are many clinical studies which have focused on the effect of restorations on periodontal tissues.^{11,12,13,20} They reported that poor marginal adaptation, deeper intracrevicular margin placement, rougher restoration surfaces, and overcontoured restorations could contribute to periodontal problems such as localized gingival inflammation, increased probing depths, and bone resorption.²¹ Especially, there is a strong correlation existed between marginal discrepancy of the restoration and gingival index, and also a significant quantitative relationship existed between the marginal discrepancy and periodontal tissue inflammation for subgingivally

located crown margins.¹¹⁻¹³ In addition, the increase of liquid monomer to powder ratio may increase the formation of pores in the polymer-based provisional prosthesis. It would act as stress risers and initiating sites for cracks, rendering the prosthesis susceptible to early fatigue fracture.³ The increase of the liquid monomer to powder ratio also reduce the mechanical strength, such as ultimate compressive strength, yield strength and compressive modulus, and induce clinical failures through stress and porosity.¹⁸ This may also leads to increased setting times.¹⁷ Hence, increased liquid monomer to powder ratio systems with high shrinkage-strain and high residual monomer should be avoided to achieve good clinical result. However, increasing amounts of activator and initiator in the system may reduce the level of the residual monomer.²² When considering modifying the liquid monomer and powder ratio of the polymer-based provisional crown and FPD materials, the effect of the change not only on the polymerization kinetics but also on other properties of the curing and cured materials must be studied in the further studies, and more number of specimens should also be tested.

CONCLUSION

Within the limitation of this study, the following conclusions were drawn.

1. Polymerization shrinkage-strain values with a liquid monomer to powder ratio of 1.0:3.0 were 4.67 %, 4.18 %, and 3.07 % for Jet, Alike, and Snap, respectively at 2 hours after the start of mixing.
2. Most shrinkage (94.3 % - 96.5 %) of the provisional crown and FPD materials investigated occurred in the first 30 minutes after the start of mixing regardless of the liquid monomer to powder ratio.
3. Increasing the liquid monomer to powder ratio induced a delayed onset of shrinkage, and

decreased the shrinkage-strain in magnitude linearly ($r = -0.769$ for Alike, -0.717 for Jet, -0.435 for Snap). The shrinkage-strain values for the ratio of 1.0:1.0 were significantly lower than those for the ratio of 1.0:3.0.

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