

IN VITRO STUDY ON EXOTHERMIC REACTION OF POLYMER-BASED PROVISIONAL CROWN AND FIXED PARTIAL DENTURE MATERIALS MEASURED BY DIFFERENTIAL SCANNING CALORIMETRY

Mun-Jeung Ko, D.D.S., M.S.D.¹, Ahran Pae, D.D.S., M.S.D.², Sung-Hun Kim, D.D.S., Ph.D.³

¹Graduate School of Clinical Dentistry, Ewha Womans University

²Assistant Professor, Department of Dentistry, Ewha Womans University

³Assistant Professor, Department of Prosthodontics, Seoul National University

Statement of problems. The heat produced during polymerization of polymer-based provisional materials may cause thermal damage to the vital pulp.

Purpose. This study was performed to evaluate the exotherm reaction of the polymer-based provisional materials during polymerization by differential scanning calorimetry and to compare the temperature changes of different types of resins.

Material and methods. Three dimethacrylate-based materials (Prottemp 3 Garant, Luxatemp Plus, Luxatemp Fluorescence) and five monomethacrylate-based material (Snap, Alike, Unifast TRAD, Duralay, Jet) were selected. Temperature changes of polymer-based provisional materials during polymerization in this study were evaluated by D.S.C Q-1000 (TA Instrument, Wilmington, DE, USA). The following three measurements were determined from the temperature versus time plot: (1) peak temperature, (2) time to reach peak temperature, (3) heat capacity. The data were statistically analyzed using one-way ANOVA and multiple comparison Bonferroni test at the significance level of 0.05.

Results. The mean peak temperature was 39.5°C (\pm 1.0). The peak temperature of the polymer-based provisional materials decreased in the following order: Duralay > Unifast TRAD, Alike > Jet > Luxatemp Plus, Prottemp 3 Garant, Snap, Luxatemp Fluorescence. The mean time to reach peak temperature was 95.95 sec (\pm 64.0). The mean time to reach peak temperature of the polymer-based provisional materials decreased in the following order: Snap, Jet > Duralay > Alike > Unifast TRAD > Luxatemp Plus, Prottemp 3 Garant, Luxatemp Fluorescence. The mean heat capacity was 287.2 J/g (\pm 107.68). The heat capacity of the polymer-based provisional materials decreased in the following order: Duralay > TRAD, Jet, Alike > Snap, Luxatemp Fluorescence, Prottemp 3 Garant, Luxatemp Plus.

Conclusion. The heat capacity of materials, determined by D.S.C., is a factor in determining the thermal insulating properties of restorative materials. The peak temperature of PMMA was significantly higher than others (PEMA, dimethacrylate). No significant differences were found among PEMA (Snap) and dimethacrylate ($P > 0.05$). The time to reach peak temperature was greatest with PEMA, followed by PMMA and dimethacrylate. The heat capacity of PMMA was significantly higher than others (PEMA, dimethacrylate). No significant differences were found among PEMA and dimethacrylate ($P > 0.05$).

Key Words

Polymer-based provisional crown and fixed partial denture materials, Differential scanning calorimetry, Heat capacity

The fabrication of provisional crowns or fixed partial dentures is a necessary procedure in fixed prosthodontic treatment. The most widely used material for the fabrication of the provisional restoration is polymer-based material. This material is set by radical polymerization reaction after mixing. During the polymerization reaction, bond-dissociation energy is released from the monomer.¹ This energy emits heat during polymerization.² The fabrication of the restoration with polymer-based materials by the direct technique imposes heat on the prepared teeth. Since the dental pulp is particularly sensitive to the elevated temperature, direct fabrication of provisional restorations may be traumatic to the prepared teeth.³ This may induce inflammatory reactions of the pulp tissue such as vascular injuries and tissue necrosis, protoplasm coagulation, expansion of the liquid in the dentinal tubules and pulp with increased outflow from the tubules.⁴ Zach and Cohen found that when external heat was applied to intact monkey teeth, a 10°F rise in the temperature of the pulp caused vitality loss in 15% of the pulp. 20°F rise caused vitality loss in 60% of the pulp, and a 30°F rise in the temperature of the pulp evoked irreversible pulpal necrosis in 100% of the pulp.⁵ Hence, in order to minimize thermal injuries of the tissue of vital teeth, dentists must be aware of the heat formation of the polymer-based materials used in dental practice.

Temperature changes from the exothermic reaction of the polymer-based provisional materials have been studied previously by various methods.^{3,5} Moulding and Teplisky³ investigated the heat produced by the provisional materials with the thermocouple. Driscoll *et al.*⁵ evaluated the exothermic release of the provisional materials by a mercury thermometer method. Kim and Watts⁶ also evaluated the exothermic reaction of contemporary polymer-based provisional materi-

als during polymerization with the thermocouple. However little data has been reported regarding the exothermic reaction of the polymer-based provisional materials measured by a differential scanning calorimetry.

The purpose of this investigation were i) to evaluate the exotherm reaction of the polymer-based provisional materials during polymerization measured by a differential scanning calorimetry and ii) to compare the temperature changes among different types of provisional materials. The null hypothesis to be tested was that there is no difference in heat generation between the monomethacrylate-based materials and the dimethacrylate-based materials.

MATERIAL AND METHODS

Eight commercially available polymer-based self-curing provisional materials were investigated in this study (Table I). Five monomethacrylate-based materials (Snap, Alike, Unifast trad, Duralay, and Jet) and three dimethacrylate-based materials (Protemp 3 Garant, Luxatemp, and Luxatemp fluorescence) were selected. Five specimens were fabricated for each material.

Temperature changes of the materials during polymerization were evaluated by DSC Q-1000 (TA Instrument, Wilmington, DE, USA) (Fig. 1). To simulate the temperature of the oral cavity, DSC Q-1000 was pre-conditioned to 37°C isothermally for 10 minutes. Each material was mixed according to the manufacturers' instructions. The mixing ratio of powder and liquid was 2:1 by volume. 20mg of polymer powder of each material were mixed with the following each liquid; Alike 8mg, Snap 8mg, Jet 7.4mg, Duralay 9mg, Unifast trad 7.4mg. The other materials were mixed by an automix dispenser tip. The mixed material was placed in a pre-weighed aluminum sample pan. The weight of pan containing the mixed material was determined by

Table I. The polymer-based provisional materials investigated

Material	Lot No.	Shade	Characteristics	Manufacturer
Alike	401051	67/B3	Monomethacrylates (PMMA)	COE, Alsip, Illinois, USA
Jet	14302040	66/A3	Monomethacrylates (PMMA)	Lang Dental Mfg. Co. Inc, Chicago, Illinois, USA
Unifast TRAD	101041	A2	Monomethacrylates (PMMA)	GC Dental Products Corp., Japan
Duralay	P:122303 L:09140L	A2	Monomethacrylates (PMMA)	Reliance Dental, Worth, Illinois, USA
Snap	90306	65/D3	Monomethacrylates (PEMA)	Parkell, Farmingdale, NY, USA
Protemp 3 Garant	156186	A3	Dimethacrylates	3M- ESPE, St Paul, MN, USA
Luxatemp Plus	512843	A2	Dimethacrylates	DMG, Hamburg, Germany
Luxatemp Fluorescence	532093	A2	Dimethacrylates	DMG, Hamburg, Germany



Fig. 1. DSC Q-1000 (TA Instrument, Wilmington, DE, USA).

reweighing the sample pan. The pan with the mixed material was transferred to DSC cell. The preparation process was finished within 30 seconds after the start of mixing. The characteristic curves were produced on a recorder chart during the setting processes of the materials. The following three measurements were determined from heat flow versus time plot: i) peak temperature, ii) time to reach peak temperature, iii) heat capacity. TA Instrument Universal Analysis 2000 (TA Instrument, Wilmington, DE, USA) was used to

calculate the three measurements. All data were statistically analyzed using one-way ANOVA and multiple comparison Bonferroni test at the significance level of 0.05. SPSS software (Version 10.1, SPSS Inc., Chicago, Ill, USA) was used for these statistical analyses.

RESULTS

The representative heat flow versus time plots of each material investigated is presented in Fig. 2.

Peak temperature was determined as the peak point on heat flow versus time plots. It was expressed as the difference between the actual maximum temperature and the pre-conditioned temperature (37°C).

Peak temperature and time to peak temperature were calculated by TA Instrument Universal Analysis 2000 when the peak point was clicked. The heat capacity of the material was the quantity of heat (cal) required to raise the temperature of 1g of the material by 1°C. The area under heat flow versus time plot was proportional to the heat of reaction. Under the heat flow versus time plot

from starting point to 600 seconds, thermal effects can be quickly identified and the heat capacity values can be determined using pre-weighed material quantities (mg). The point of 600 seconds was assumed to be the time to reach the equilibrium heat flow state in all investigated materials.

1. Peak temperature

The results for peak temperature are presented in Table II and Fig. 3. The peak temperature of the

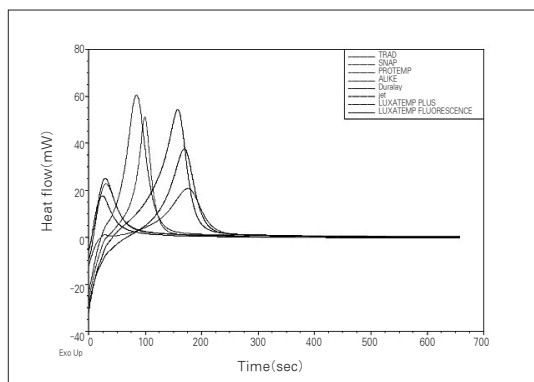


Fig. 2. The representative heat flow versus time plots of the polymer-based provisional materials.

Table II. Mean (standard deviation) of peak temperature of the polymer-based provisional materials investigated

Material	Peak temperature (°C)	
	Mean	SD
Alike	40.5	0.3
Jet	39.6	0.2
Unifast TRAD	40.47	0.5
Duralay	41.1	0.3
Snap	38.6	0.1
Protemp 3 Garant	38.7	0.3
Luxatemp Plus	38.9	0.3
Luxatemp Fluorescence	38.4	0.1

polymer-based provisional materials decreased in the following order: Duralay (41.1°C) > Unifast trad (40.5°C) > Alike (40.5°C) > Jet (39.6°C) > Luxatemp plus (38.9°C) > Protemp 3 Garant (38.7°C) > Snap (38.6°C) > Luxatemp fluorescence (38.4°C). The one-way ANOVA test demonstrated statistically significant differences between materials ($P < 0.05$). A multiple comparison *Bonferroni* test showed that no significant differences were found between Alike and Unifast trad ($P > 0.05$). Luxatemp plus, Protemp 3 Garant, Snap, Luxatemp fluorescence were comparable ($P > 0.05$). The mean peak temperature of the monomethacrylates was 40.0°C (± 0.9) and that of the dimethacrylates was 38.6°C (± 0.3). Its difference was significant ($P < 0.05$).

2. Time to peak temperature

The results for time to reach peak temperature are presented in Table III and Fig. 4. The mean time to reach peak temperature of the polymer-based provisional materials decreased in the following order: Snap (177.9 sec) > Jet (175.1 sec) > Duralay (157.9 sec) > Alike (98.2 sec) > Unifast Trad (79.7 sec) > Luxatemp plus (27.5 sec) > Protemp

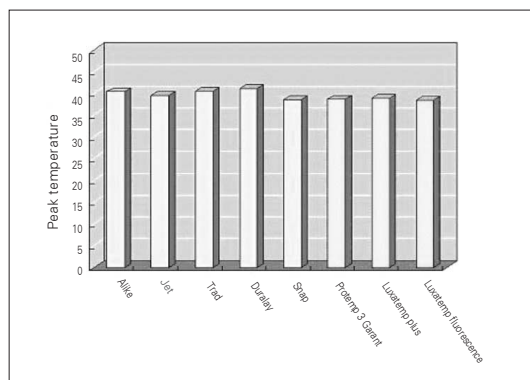


Fig. 3. Peak temperature (°C) of the materials investigated.

3 Garant (25.7 sec) > Luxatemp fluorescence (25.6 sec). The one-way ANOVA test demonstrated statistically significant differences between materials ($P < 0.05$). A multiple comparison *Bonferroni* test showed that no significant differences were found between Jet and Snap ($P > 0.05$). Protemp 3 Garant, Luxatemp plus, Luxatemp fluorescence were comparable ($P > 0.05$). The mean time to peak temperature of the monomethacrylates and the dimethacrylates were 137.8 sec (± 42.4) and 26.3 sec (± 2.8) respectively. The value of the monomethacrylates was significantly higher than that of the dimethacrylates ($P < 0.05$).

Table III. Mean (standard deviation) of time to reach peak temperature of the polymer-based provisional materials investigated

Material	Time (sec)	
	Mean	(SD)
Alike	98.2	(4.1)
Jet	175.1	(9.2)
Unifast Trad	79.7	(12.3)
Duralay	157.9	(7.3)
Snap	177.9	(6.3)
Protemp 3 Garant	25.7	(3.9)
Luxatemp plus	27.5	(0.9)
Luxatemp fluorescence	25.6	(2.9)

Table IV. Mean (standard deviation) of heat capacity produced by the polymer-based provisional materials investigated

Material	Heat capacity(J/g)	
	Mean	SD
Alike	335.9	12.7
Jet	383.7	32.0
Unifast TRAD	399.9	84.0
Duralay	414.9	44.8
Snap	220.3	30.4
Protemp 3 Garant	178.5	31.7
Luxatemp Plus	176.9	32.5
Luxatemp Fluorescence	187.6	31.2

3. Heat capacity

The results for heat capacity are presented in Table IV and Fig. 5. The heat capacity of the polymer-based provisional materials decreased in the following order: Duralay (414.9J/g) > TRAD (399.9J/g) > Jet (383.7J/g) > Alike (335.9J/g) > Snap (220.3J/g) > Luxatemp Fluorescence (187.6J/g) > Protemp 3 Garant (187.5J/g) > Luxatemp Plus (176.9J/g). The one-way ANOVA test demonstrated statistically significant differences between materials ($P < 0.05$). A multiple comparison *Bonferroni* test showed that no significant differences were found among Unifast TRAD, Jet

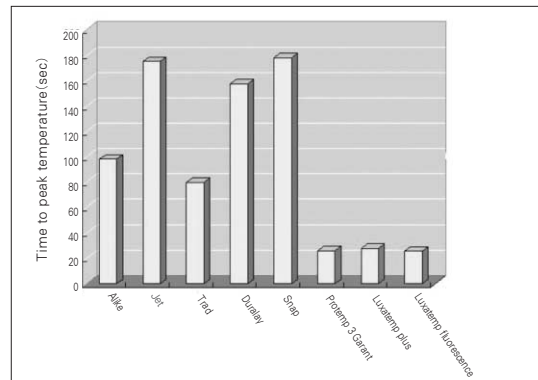


Fig. 4. The time to reach peak temperature (sec).

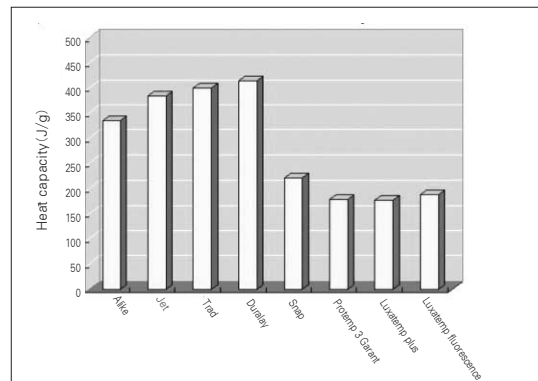


Fig. 5. Heat capacity.

and Alike ($P > 0.05$). Snap, Protemp 3 Garant, Luxatemp Plus, Luxatemp Fluorescence were comparable ($P > 0.05$). The mean heat capacity of the monomethacrylates (350.9J/g) was significantly higher than that of the dimethacrylates (181.0J/g) respectively ($P < 0.05$).

DISCUSSION

Eight self-curing polymer-based provisional materials were investigated in this study. Five monomethacrylate-based materials (Snap, Alike, Unifast TRAD, Duralay, and Jet) and three dimethacrylate-based materials (Protemp 2 Garant, Luxatemp Plus, and Luxatemp Fluorescence) were selected. The temperature at which the specimens were polymerized was 37 °C to simulate the temperature of the oral cavity. The temperature change was recorded by DSC Q-1000. It should be emphasized that the differential scanning calorimetry instrument (DSC), working under isothermal conditions, measures the quantity of heat removed from or put into a test material in order to keep it at the same constant temperature as the reference sample pan. DSC instrument is capable of being used isothermally at any pre-set temperature in which case a plot is obtained as a recorder of rate of heat output or input against time. If chemical reaction is carried out at constant temperature, a peak is obtained on the recorder trace. The area under the peak is proportional to the heat of reaction. McCabe and Wilson¹¹ established that DSC is a suitable method for evaluation of setting characteristics of cavity lining, restorative, and temporary crown and bridge materials. Also, the heat capacity of materials, determined by D.S.C., is a factor in determining the thermal insulating properties of restorative materials. The advantages of D.S.C were to permit the direct measurement of specific heat and to determine heat content

changes by integration of the specific heat function clearly¹⁴.

The mean peak temperature of all materials was 39.5°C (± 1.0). The amount of exothermic heat during polymerization depends upon the volume of materials.¹⁹ Thus, there are differences in the peak temperature according to methods. The mean peak temperature of the monomethacrylates (40.0°C) was significantly higher than that of the dimethacrylates (38.6°C), and in the monomethacrylate group the peak temperature of PMMA was significantly higher than that of the PEMA. This is in accordance with the study of Moulding and Teplisky.³ However, in this study, the peak temperature of PEMA was lower than that of dimethacrylate. Driscoll *et al.*⁵ concluded that the temperature increase produced by PMMA was statistically higher than that of the vinyl ethyl methacrylate, urethane dimethacrylate and bisacryl composite resin. This finding agrees with a previous report in which it was found that the peak temperature on polymerization can be reduced by substitution of higher molecular weight methacrylates for methylmethacrylate.¹⁸ On the other hand, Kim and Watts⁶ concluded that the dimethacrylate-based materials (except for fast setting material) exhibited no significant differences in peak temperature and total peak area from the monomethacrylate-based materials. This can be explained by the mixing ratio of the constituents and different ambient temperature.^{2,18} The mixing ratio of monomethacrylates and ambient temperature they used were 3:1 (powder:liquid) by volume and 23°C respectively. But in this study, the mixing ratio of the monomethacrylates and ambient temperature used were 2:1 (powder:liquid) by volume and 37°C respectively. Haas *et al.*¹⁶ showed that by increasing the powder to liquid ratio, i.e. decreasing the volume of monomer, the peak temperature was reduced considerably. The exothermic reaction of the polymer-based

provisional materials in vitro finding was evaluated in this study. But from the clinical point of view, the heat formation on the resin surface and its dissipation at the interface between dentin and resin were more important than the peak temperatures during polymerization. Therefore the results of in vitro studies on peak temperatures did not correlate exactly with in vivo finding. An intrapulpal temperature rise of 5.5°C (10 °F) in rhesus Macaca monkeys caused 15% of the pulps to lose vitality according to the histologic studies of Zach and Cohen.⁷ However, they investigated thermal change in intact teeth. In clinical situations, the dentinal surface was exposed after tooth preparation. The dentin is usually vital and contains protoplasmic extensions of cells. The different properties of the organic structure in the tubules of vital and non-vital teeth and the effect of circulation of dentinal fluids must be considered. The condition and quality of the pulpal vascular structures may determine the degree of damage from thermal trauma.⁴⁸ In addition, the thickness of the residual dentin is a critical factor in reducing thermal transfer to the pulp because of its low thermal conductivity.^{9,15} If fabrication of provisional restorations by direct technique is preferred, precautionary measures must be used to minimize temperature increase of the tooth structure from the exothermic reaction of the resins. The temperature rise may be reduced by using air and water coolant or irrigating the restorations with cool water and by using a matrix material that can dissipate the heat rapidly.⁸

The mean time to reach peak temperature was 95.95 sec (\pm 64.0). The time to reach the peak temperature of the monomethacrylates (137.8 sec) was significantly longer than that of the dimethacrylates (26.3 sec). The differences in the time to reach peak temperature were statistically significant for the three group resins (PMMA, PEMA and dimethacrylate). This can be explained by the

slower onset of the reaction for the methacrylates. This result was in well accordance with the result of Kim and Watts.⁶ However, if polymerization took place at a higher temperature, the peak temperatures were attained at a faster time.¹⁷ Therefore, the time to reach peak temperature in this study (95.5sec) was faster than the time in the result of Kim and Watts (241.0sec). Attention should be paid to prevent tooth structure from potential damage during that period. The dimethacrylate-based materials were preferable because the faster setting reaction can reduce the fabrication time.²⁰ It is necessary for the provisional restoration to be removed from the mouth, cooled in water, and then reinserted onto the prepared tooth several times during polymerization.¹⁰

The mean heat capacity was 287.2 J/g (\pm 107.68). The mean heat capacity of the monomethacrylates and the dimethacrylates were 350.9 J/g and 181.0 J/g, respectively. This meant that more energy was required to increase the temperature of the monomethacrylates than that of the dimethacrylates. No significant differences were found between the PEMA and the dimethacrylates. Little data have been reported regarding comparison of heat capacity of multiple polymer-based provisional materials. Thus, comparison of this result with other studies was difficult.

A number of resin materials are available for the fabrication of provisional restorations. One of the oldest acrylic resins is polymethylmethacrylate (PMMA). It remained popular as a provisional restoration material due to its ease of manipulation, smooth surface, and cost. However the residual free monomer in the setting materials was toxic to vital pulp tissue and the exothermic reaction occurring during polymerization may damage the pulp and periodontal tissue.²¹⁻²³ Dimethacrylate materials have been developed

which produce less chemical and exothermic irritation to the pulp and periodontal tissue. Advantages of the dimethacrylate included the ease of manipulation, low exothermic reaction and decreased polymerization shrinkage. However there are disadvantages of these materials including poor surface polish, increased cost and frequent fracture.²¹⁻²³ Understanding of not only structural characteristics of the provisional materials, but also exothermic reaction may offer significant advantages in clinical performance of the materials. Also visible-light activated resin was found to produce a temperature rise significantly lower than that of other polymer-based provisional materials.⁵ However, this aspect was not included in this study and requires further investigation.

CONCLUSION

Within the limitations of this study, the following conclusions were drawn:

1. The mean peak temperature was 39.5°C (\pm 1.0). The peak temperature of the polymer-based provisional materials decreased in the following order: Duralay > Unifast TRAD, Alike > Jet > Luxatemp Plus, Protemp 3 Garant, Snap, Luxatemp Fluorescence. The peak temperature of monomethacrylate was significantly higher than that of dimethacrylate ($P < 0.05$).
2. The mean time to reach peak temperature was 95.95 sec (\pm 64.0). The mean time to reach peak temperature of the polymer-based provisional materials decreased in the following order: Snap, Jet > Duralay > Alike > Unifast TRAD > Luxatemp Plus, Protemp 3 Garant, Luxatemp Fluorescence. The time to reach peak temperature of the monomethacrylates was significantly longer than that of the dimethacrylates ($P < 0.05$).
3. The mean heat capacity was 287.2 J/g (\pm 107.68). The heat capacity of the polymer-

based provisional materials decreased in the following order: Duralay > Unifast TRAD, Jet, Alike > Snap, Luxatemp Fluorescence, Protemp 3 Garant, Luxatemp Plus. Heat capacity of the monomethacrylates was significantly higher than that of the dimethacrylates ($P < 0.05$).

REFERENCES

1. Billmeyer F.W. Textbook of Polymer Science. John Wiley & Sons, New York. 1984. p.71.
2. Vallittu PK. Peak temperature of some prosthetic acrylates on polymerization. *J Oral Rehabil* 1996;23:776-81.
3. Moulding MB, Teplisky PE. Intrapulpal temperature during direct fabrication of provisional restoration. *Int J Prosthodont* 1990;3:299-304.
4. Nyborg H, Brännstrom J. Pulp reaction to heat. *J Prosthet Dent* 1968;19:605-12.
5. Driscoll CF, Woolsey G, Ferguson WM. Comparison of exothermic release during polymerization of four materials used to fabricate interim restoration. *J Prosthet Dent* 1991;65:504-6.
6. Kim SH, Watts DC. Exotherm behavior of the polymer-based provisional crown and fixed partial denture materials. *Dental Mater* 2004;20:383-7.
7. Zach L, Cohen G. Pulp response to externally applied heat. *Oral Surg* 1965;19:515-30.
8. Tjan AHL, Grant BE, Godfrey MF. Temperature rise in the pulp chamber during fabrication of provisional crowns. *J Prosthet Dent* 1989;62:622-6.
9. Craig RG. Restorative dental materials. 7th ed. St Louis: CV Mosby Co, 1985:48,506.
10. Grajower R, Shaharbani S, Kaufman E. Temperature rise in pulp chamber during fabrication of temporary self-curing resin crowns. *J Prosthet Dent* 1979;41:535-40.
11. McCabe JF, Wilson. The use of differential scanning calorimetry for the evaluation of dental materials. *J Oral Rehabil* 1995;7:103-10.
12. Moulding MB, Loney RW. The effect of cooling techniques on intrapulpal temperature during direct fabrication of provisional restorations. *Int J Prosthodont* 1991;4:332-36.
13. Stanley HR. Pulpal response to dental techniques and materials. *Dent Clin North Am* 1971;15:115-26.
14. O' Neill MJ. Measurement of specific heat functions by differential scanning calorimetry. *Analytical Chemistry* 1966;38:1331-6.
15. Brown WS, Dewey WA, Jacobs MR. Thermal properties of teeth. *J Dent Res* 1970;49:752-5.
16. Haas SS, Brauer GM, Dickson G. A characterization of polymethyl methacrylate bone cement. *J Bone and Joint Surgery* 1975;57:380.

17. Migliaresi C, Fambri L, Kolarik A. Polymerization kinetics, glass transition temperature and creep of acrylic bone cements. *Bio Materials* 1994;15:875.
18. Brauer CF, Steinberger DR, Stansbury JW. Dependence of curing time, peak temperature, and mechanical properties on the composition of bone cement. *J Biomed Mater Res* 1986;20:839.
19. Wolcott RB, Paffenbarger GC, Schoonover IC. Direct resinous filling materials-temperature rise during polymerization. *J Am Dent Assoc* 1951;42:253-63.
20. John OB, Carl WH, Cliff B. Evaluation of resins for provisional restorations. *Am J of Dent* 1992;5:137-9.
21. Kaiser DA, Cavazos E. Temporization technique in fixed prosthodontics. *Dent Clin North Am* 1985;29:403-12.
22. Krug RS. Temporary resin crowns and bridges. *Dent Clin North Am* 1975;19:313-20.
23. Lui JL, Sectos JC, Phillips RW. Temporary restorations. *Oper Dent* 1986;11:103-10.

Reprint request to:

SUNG-HUN KIM D.D.S., PH.D.

DEPARTMENT OF PROSTHODONTICS, GRADUATE SCHOOL

SEOUL NATIONAL UNIVERSITY

28-1, YEONGUN-DONG, CHONGNO-GU, SEOUL, 10-749, KOREA

ksh1250@snu.ac.kr