

原 著

Exothermic Setting Behaviour in Dental Investment and Gypsum (Thermoanalytical Method)

Kunio Wakasa, Hidenori Urabe*, Yasuhiro Yoshida**, Atsuharu Ikeda and Masao Yamaki

(Received for publication, April 5, 1994)

ABSTRACT

Setting properties were measured by thermoanalytical method due to differential scanning calorimetry (DSC) in dental cast investments and gypsums. The heat for setting (hardening) at isothermal mode was calculated using DSC curves with initial setting and final setting times, and also the time at a peak on DSC curves (peak time) was found between the times. Setting time at a penetration test agreed with final setting time on DSC analysis. The results show that DSC behaviour of dental cast investments and gypsums is measured analogously to curing performance at isothermal temperature of dental composite restoratives, showing that there appears the setting on the thermal analysis curve.

INTRODUCTION

The setting reaction of gypsum-bonded and phosphate-bonded investments is exothermic associated with expansion¹⁻³. Similar characteristics are also observed for gypsum (calcium sulfate hemihydrate)^{4,5}. The measurement was done using a thermocouple¹⁻³ and a galvanometer³. Setting reaction of the mixed materials occurred as a total thermal change within the materials.

Thermal behaviour in dental resin materials was examined by differential scanning calorimetry (DSC)⁶⁻⁸, so DSC was applied to measure thermal change during the setting of dental investments and gypsums. Conventionally a penetration test was carried out using a Vicat needle to measure a setting time⁴.

This study examined thermal properties of dental investments and gypsums by measuring thermal change in DSC curves, and also compared with setting time at a penetration test.

MATERIALS AND METHODS

The materials tested were two gypsum-bonded investments (GC; Cristobalite investment P and GQ; OK powder, GC Co, Tokyo), one phosphate-bonded investment (PC; Ceravest G, Shofu Inc, Kyoto) and two gypsums (FP; Maruishi plaster, Maruishi, Tokyo and KP; New plaster, GC Co, Tokyo). The materials were prepared for testing by mixing powders with water. The ratio water/powder was 0.32 (GC and GQ) and 0.24 (PC investment), and 0.50 (FP) and 0.24 (KP gypsum).

The thermal properties investigated were (1) time to peak temperature (P), (2) final setting time (F), and (3) heat for setting (H) in DSC measurement. In a conventional penetration test setting time (S) is defined as the time elapsing from the start of mixing until the point of a Vicat needle will no longer penetrate the surface of the test material⁴. Thermal analysis was performed using a DSC (Shimadzu DT30, and DT50, Kyoto). Each mixed investment material with a liquid (30 mg) was weighed out into an aluminum sample pan (1.5 mm height × 6 mm diameter) which was hermetically sealed by mechanically crimping. For the mixed gypsums a pan with 5 mm (height) × 6 mm (diameter) was used. All experiments were carried out at constant temperature of 20°C beginning at 1 min after placing the sample in the pan. The

Hiroshima University School of Dentistry, Department of Dental Materials (Chairman; Professor Masao Yamaki).

*Hiroshima University School of Dentistry, Department of Operative Dentistry (Chairman; Professor Hideaki Shintani).

** Hiroshima University School of Dentistry, Department of Removable Prosthodontics (Chairman; Professor Yasumasa Akagawa).

Correspondence to *Dr K. Wakasa*; Hiroshima University School of Dentistry, Department of Dental Materials, Kasumi 1 chome, Minamiku, Hiroshima City, 734 Japan.

difference in temperature between the pan containing mixed sample and a reference (empty pan) was measured. The value was calibrated using pure gallium of heat for fusion = 82.3 J/g (Mp, 29.93 °C). For the penetration test a steel casting ring (40 mm height and 30 mm diameter), which was lined with a dry lining material (Kaolin, Dentsply Co, York, USA) and placed on a glass slab, was used. On the contrary, the gypsum was poured into the ring without a lining material. The test was done for 7 specimens of each investment and gypsum.

RESULTS

Unmixed material with water had no thermal change after mixing (Fig. 1), because only powder did not occur setting reaction. Setting reaction occurred in Figs. 2

(investment) and 3 (gypsum) when mixed with water. In a typical example of exothermic heattime relationship (Fig. 3) the peak (Pe) was observed after the time (I; initial setting time) when initial setting started, and the temperature in each mixed powder lowered after the peak was reached to F (final setting time). Each mixed powder followed a similar pattern with a peak and a gradual decline.

The mean and standard deviation values of P, F, and H in DSC analysis were given in Table 1 (investment and gypsum). P mean value was 3.6 (GC), 3.8 (GP) and 4.6 min (PC) for investment, and 8.3 (FP) and 6.2 min (KP) for gypsum. F was greater in gypsum (35.0, 37.0 min) than in investment (6.7, 6.7, 8.1 min) and also H value (J/g) became greater about 10 times in gypsum than

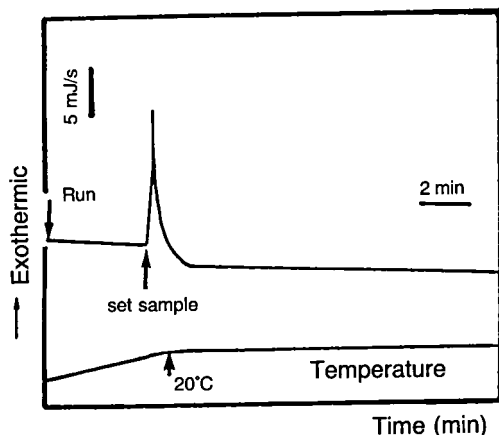


Figure 1 DSC curve and temperature change when only powder without liquid was prepared.

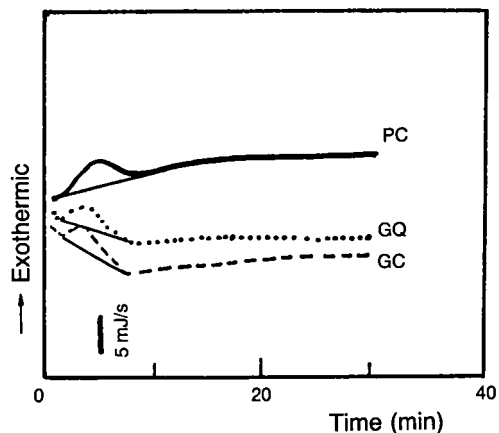


Figure 2 DSC curves of investments GC, GQ and PC.

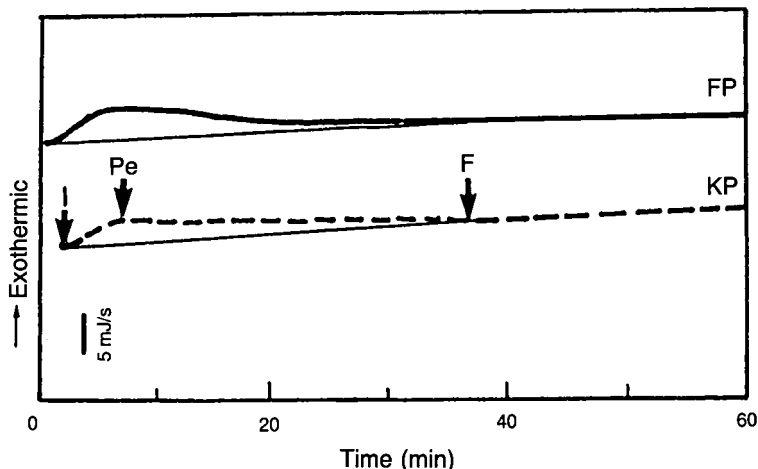


Figure 3 DSC curves of gypsums FP and KP. See text for key.

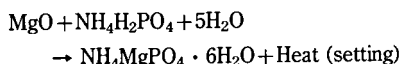
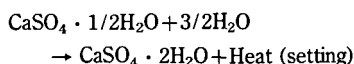
Table 1 DSC analysis of investments (GC, GQ, PC) and gypsums (FP, KP); Mean value and standard deviation of peak time (P), final setting time (F) and heat for setting (H).

Code	Results		
	P (min)	F (min)	H (J/g)
GC	3.6 (0.3)	6.7 (0.2)	14.3 (1.2)
GQ	3.8 (0.4)	6.7 (0.2)	12.4 (1.0)
PC	4.6 (0.2)	8.1 (0.4)	16.9 (3.0)
FP	8.3 (0.5)	35.0 (2.4)	117.4 (5.0)
KP	6.2 (1.5)	37.0 (1.6)	105.6 (3.6)

investment. There was no significant difference of P, F and H between investments or gypsums ($p > 0.05$). On the contrary, penetration results of gypsums and investments showed that S was 35.0 ± 4.2 (FP), 32.0 ± 3.0 (KP) for gypsum and 7.5 ± 1.0 (GC), 7.2 ± 0.5 (GQ) and 9.0 ± 0.1 min (PC) for investment. The value of S in penetration test is significantly higher than P value in DSC ($p < 0.05$), but F values in investments and gypsums showed the almost same magnitudes as S values.

DISCUSSION

In this work of investment and gypsum it is clear that the setting time as measured by a penetration test gives a result close to that obtained by taking the time to reach the end of the exotherm in DSC test. In other words the values of F (thermal analysis) closely approximated those of S (a penetration test). Considering the difference in setting obtained by DSC analysis and the penetration test, a possible expansion gives a variation of temperature at different locations within the casting ring. Pure gallium (heat for fusion; 82.3 J/g) was used for the calibration of heat for setting of dental materials. The reason is that the temperature changed approximately from 22 to 66°C for phosphate-bonded investment^{2,9} and approximately 0 to 40°C for gypsum-bonded investment and gypsum^{4,5}. Setting reaction of the samples was measured during calcium sulfate dihydrate formed in gypsum ones¹⁰, or magnesia and H₂O reacted with phosphate powder in phosphate-bonded investment¹¹ as the following results;



That is, the setting reaction was clarified by measuring thermal change as Heat (setting) by means of DSC analysis. Thermal change gives initial and final setting time and also heat for setting at isothermal temperature range. The values of heat for setting measured by thermocouple method were 96.3 and 118.2 J/g for gypsum¹² and 21.4 J/g for investment⁵, indicating that the values were in good agreement with the results in Table 1. The compositions related to thermal change due to chemical reaction with H₂O are gypsum in gypsums and gypsum-bonded investments and magnesia and phosphate powders in phosphate-bonded type. This DSC behaviour was also clarified for ethyl silicate-bonded investments¹³⁻¹⁵. DSC measurement of dental gypsums and investments gives an indication of setting characteristics with heat for setting.

SUMMARY

DSC measurement in dental cast investment and gypsum exhibited setting characteristics in relation to heat change due to temperature change. It was analogous to curing performance in dental composite resins at isothermal temperature, representing that setting reaction occurred associated with the formation of CaSO₄ · 2H₂O or NH₄MgPO₄ · 6H₂O. Thermoanalytical study clearly measured heat for setting in cast investment and gypsum, and also setting time in penetration test.

ACKNOWLEDGEMENTS

The authors gratefully wish to express the deep appreciation to the use of "Biomaterial Combined Analysis System", which was supported as Heisei 5-nen-do Hiroshima Daigaku Daigakuin Sai-sentan Setsubih (Hiroshima University Graduate School, The latest Grant-in-Aid, 1993) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

- 1) Watanabe, M.: Study on phosphate bonded investments. Part III. Relationship between composition and strength and properties of experimentally produced investments. *Kou Byou Shi* 36, 215-222, 1969.
- 2) Marsaw, F. A., de Rijk, W. G., Hesby, R. A., Hinman, R. W. and Pelleu, G. B.: Internal

- volumetric expansion of casting investments. *J. Prosthet. Dent.* 52, 361-366, 1984.
- 3) Stevens, L., Okamoto, A. and Jørgensen, K. D.: Dimensional change. in mould space on setting of phosphatebonded investment. *Aust. Dent. J.* 30, 281-284, 1985.
 - 4) Phillips, R. W.: *Skinner's Science of Dental Materials*, 9 th edn, W. B. SAUNDERS Co, Philadelphia, pp 69-91, 1991.
 - 5) Nakamura, M.: Influence of various enviromental temperatures on setting procedure and physical properties of cristobalite investment. *Shika Rikougaku Zasshi* 18, 33-45, 1977.
 - 6) McCabe, J. F. and Wilson, H. J.: The use of differential scanning calorimetry for the evaluation of dental materials. *J. Oral Rehabil.* 7, 103-110, 1980.
 - 7) Antonucci, J. M. and Toth, E. E.: Extent of polymerization of dental resins by differential scanning calorimetry. *J. Dent. Res.* 62, 121-125, 1983.
 - 8) Lee, H. and Colby, C.: Heat of polymerization of nine mono, di, and trimethacrylate esters tested neat and with low levels of peroxide by dynamic diffrential scanning calorimetry. *Dent. Mater.* 2, 175-178, 1986.
 - 9) Finger, W. and Kota, K.: A modified phosphate-bonded casting investment. *Scand. J. Dent. Res.* 90, 243-248, 1982.
 - 10) Mori, T: Thermal behavior of the gypsum binder in dental casting investments. *J. Dent. Res.* 65, 877-884, 1986.
 - 11) Allan, F. C. and Asgar, K.: Reaction of Cobalt-Chromium casting alloy with investment. *J. Dent. Res.* 45, 1516-1528, 1966.
 - 12) Sakai, T.: Binderless silica investments for dental casting. *Nihon Shika Zairyou Kikai Gakkai Zasshi* 26, 1-12, 1972.
 - 13) Wakasa, K. and Yamaki, M.: Application of silica-sol investment to dental ceramics. *J. Mater. Sci. Letters* 12, 1897-1899, 1993.
 - 14) Wakasa, K., Ikeda, A., Yoshida, Y. and Yamaki, M.: Silica investment prepared for dental purposes: effect of cristobalite content on mechanical properties. *J. Mater. Sci. Letters* 12, 1908-1910, 1993.
 - 15) Wakasa, K., Yoshida, Y., Ikeda, A. and Yamaki, M.: Effect of gelation on setting time in ethyl silicate-bonded investment. *J. Mater. Sci. Letters* 13, 258-259, 1994.