

## Differential Scanning Calorimetric Study of Acrylic Resin Powders Used in Dentistry

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The thermal behavior of eight dental acrylic resin powders was studied using differential scanning calorimetry (DSC). In addition, high performance liquid chromatography was performed to supplement the DSC analysis. The HPLC analysis revealed that the contents of residual monomers and benzoyl peroxide (BPO) in the powders were 0.01-0.97 mass% and 0.25-1.28 mass%, respectively. All the resin powders produced one broad exothermic peak, while a mixture of BPO and PMMA powders generated two peaks. One peak pattern was assigned to the decomposition of BPO included within the polymer particles. The results suggested that BPO was present inside the particles and little BPO was mixed into the resin powders. Moreover, the present study demonstrated a unique useability of DSC in characterizing resin powders.

Key words : DSC, Acrylic resin, PMMA

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### INTRODUCTION

Acrylic resins of liquid methyl methacrylate (MMA) and polymethacrylates powder, usually poly(methyl methacrylate) (PMMA), have been clinically used for a long time in dentistry. However, little information on the resins has been provided from the manufacturers. Moreover, few characterization studies on the dental resins have been published in recent years<sup>1)</sup>. Thus, in this study, as part of a characterization study, we tried to characterize the thermal behavior of the powder component of commercial dental resins using differential scanning calorimetry (DSC). Additionally, high performance liquid chromatography (HPLC) was also done to supplement the DSC analysis.

DSC has been used in dental material research mainly for studying the polymerization or setting reactions of dental resins<sup>2-6)</sup> and for measuring glass transition temperatures of moulded denture base polymers<sup>7)</sup>, but not for characterizing acrylic resin powders.

### MATERIALS AND METHODS

#### *Materials*

The eight dental resin powders used are summarized in Table 1. In addition, a PMMA without benzoyl peroxide (BPO), MB-8C (Lot. No. FJ-8317, Sekisui, Osaka),

Table 1 Dental acrylic resin powders studied

Resin	Lot No.	Manufacturer
Acron	FJ21	GC
Unifast II	160351	GC
Metafast	80501	Sun Medical
Repairsin	040851	GC
Mild Rebaron	251061	GC
Tokuso rebase	525778	Tokuso
Soft liner	030981	GC
Denture liner	109705	Shofu

was analyzed for comparison. BPO (Nakarai tesque, Kyoto) was purified by recrystallization from acetone/water before use.

#### *Differential scanning calorimetry (DSC)*

DSC was performed with a DSC 3100 equipped with a thermal analysis processing system 1000 (MAC Science, Yokohama). A sample of 10 mg was placed in an aluminum pan at room temperature and then heated at 20°C/min to 200°C in air (first run). It was then cooled to room temperature and heated again at 20°C/min to 200°C (second run). Exothermic heat was calculated by integration of DSC after tentatively establishing a baseline between the bottom of DSC at 110-130°C and a point at 180°C. All samples were measured in duplicate.

#### *High performance liquid chromatography (HPLC)*

A sample of 50 mg was dissolved in 1 ml of acetone and then 10 ml of methanol was added to the solution to precipitate the polymer. The supernatant of the solution was filtered through a 0.45 µm pore Millipore filter. HPLC analysis was performed using a JASCO system (GULLIVER 1500, JASCO, Tokyo), equipped with a CAPCELL PAK C18 column (UG120, 4.6 mm×250 mm, Shiseido, Tokyo), a diode array detector (MD-1510) (detection at  $\lambda = 230$  nm). Ten µl of the sample solution was injected and analyzed at 40°C at a flow rate of 1.0 ml/min with acetonitrile/water (50/50%).

## RESULTS AND DISCUSSION

Fig.1 shows typical DSC thermograms obtained on the first and the second runs. The sample produced one broad exothermic peak in DSC and one sharp  $\Delta$ DSC (differential of DSC) peak on the first run (A). However, the thermogram obtained on the second scan showed no exothermic peak, but only a glass transition pattern (B). All the resin powders analyzed in the present study demonstrated a similar thermogram to that shown in Fig.1, although the exothermic peak heights or areas had variations among the powders.

A possible explanation for the exothermic peak observed in the resin powders

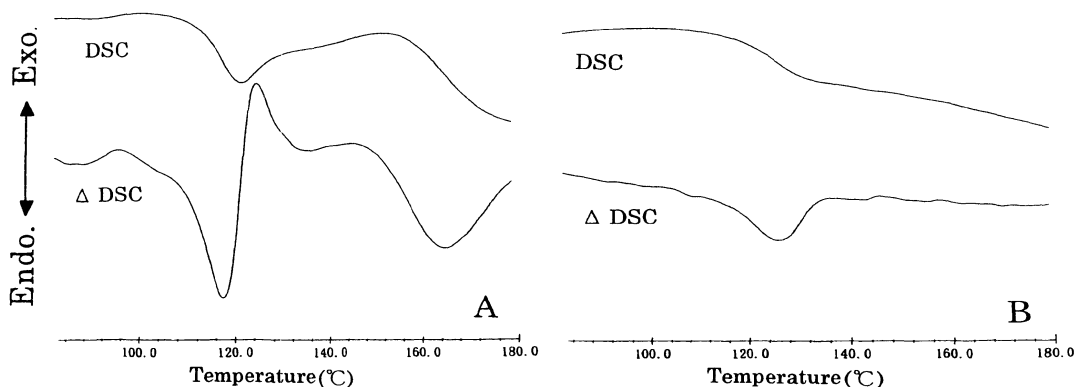


Fig. 1 Typical DSC thermograms for Acron.  
A, first run; B, second run

Table 2 Contents of methyl methacrylate (MMA), ethyl methacrylate (EMA) and benzoyl peroxide (BPO)  
(mass%)

Resin	MMA	EMA	BPO
Acron	0.97	—	0.65
Unifast II	0.42	0.11	0.69
Metafast	0.07	0.12	0.88
Repairsin	0.04	0.31	1.28
Mild Rebaron	0.01	0.32	0.87
Tokuso rebase	—	0.22	0.73
Soft liner	—	0.15	0.25
Denture liner	—	0.01	0.79

was due to the decomposition of benzoyl peroxide (BPO) and/or polymerization of residual monomers remaining within the polymer particles.

To examine this hypothesis, we first determined the amounts of BPO and monomer in the powders using high performance liquid chromatography (HPLC). The results are summarized in Table 2. The amounts of BPO and monomer contained in the powders were 0.25-1.28 mass% and 0.01-0.97 mass%, respectively. Accordingly, the origin of the exotherm could have been the BPO and/or monomer. However, regression analyses suggested that the exotherm observed could primarily be due to BPO, because there was a good correlation between the BPO content determined by HPLC and the exothermic heat (Fig. 2)(correlation coefficient  $r=0.89$ ), but a poor correlation between the monomer content and the exothermic heat (correlation coefficient  $r=0.24$ ) was demonstrated. However, the residual monomer could also contribute to the exotherm to some degree, depending on its content in the powder. Actually, a PMMA powder containing a relatively large amount of MMA (0.97%) appeared to generate a little more heat than expected from the linear regression line shown in Fig. 2, deviating upwards from the line.

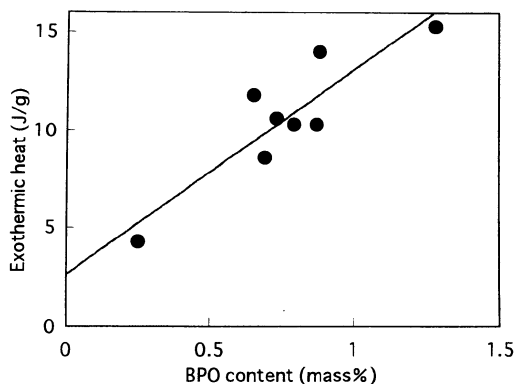


Fig. 2 Correlation between BPO content determined by HPLC and exothermic heat in the temperature range of 120-180°C.

Secondly, we examined the effect of the presence of BPO in PMMA powders on the DSC pattern. Fig. 3 shows the change in DSC pattern before and after the addition of 1 or 2 mass% of BPO to a BPO-free PMMA and a dental resin powder. The BPO-free PMMA alone produced no exothermic peak, only a glass transition pattern. The addition of BPO to the BPO-free PMMA resulted in a drastic change in the DSC pattern (Figs. 3A and B); two exothermic peaks in DSC and two sharp peaks in  $\Delta$ DSC were observed (two peak pattern). A similar change in the DSC pattern was also observed in the dental resin powder including BPO within the particles by the addition of BPO (Figs. 3C and D). The two peak pattern could be interpreted as a result of overlapping of melting (corresponding to an endothermic peak observable at 108°C) and decomposition of BPO, and the glass transition of PMMA.

The DSC thermogram shown in Fig. 3B is quite different from that in Fig. 3C, in which one exothermic peak in DSC and one sharp peak in  $\Delta$ DSC are noticeable (one peak pattern). This means that each powder analyzed in Figs. 3B and 3C produced a different DSC pattern, despite both powders containing BPO. A plausible explanation for this difference is: (1) a mixture of PMMA and BPO existing outside PMMA particles produces the two peak pattern because both melting and decomposition of the free BPO are observable in DSC; (2) PMMA including BPO inside the particles generates only one peak because melting of BPO molecules dispersed or dissolved in the PMMA matrix is unlikely to occur, and only the decomposition is observable in DSC.

A sharp peak observed at about 114°C in  $\Delta$ DSC was most characteristic of free BPO present outside PMMA particles. Therefore, its peak could be used to differentiate whether BPO exists inside or outside PMMA particles, and to determine the amounts of outside BPO.

Actually, it was found that the peak height was proportional to the amount of

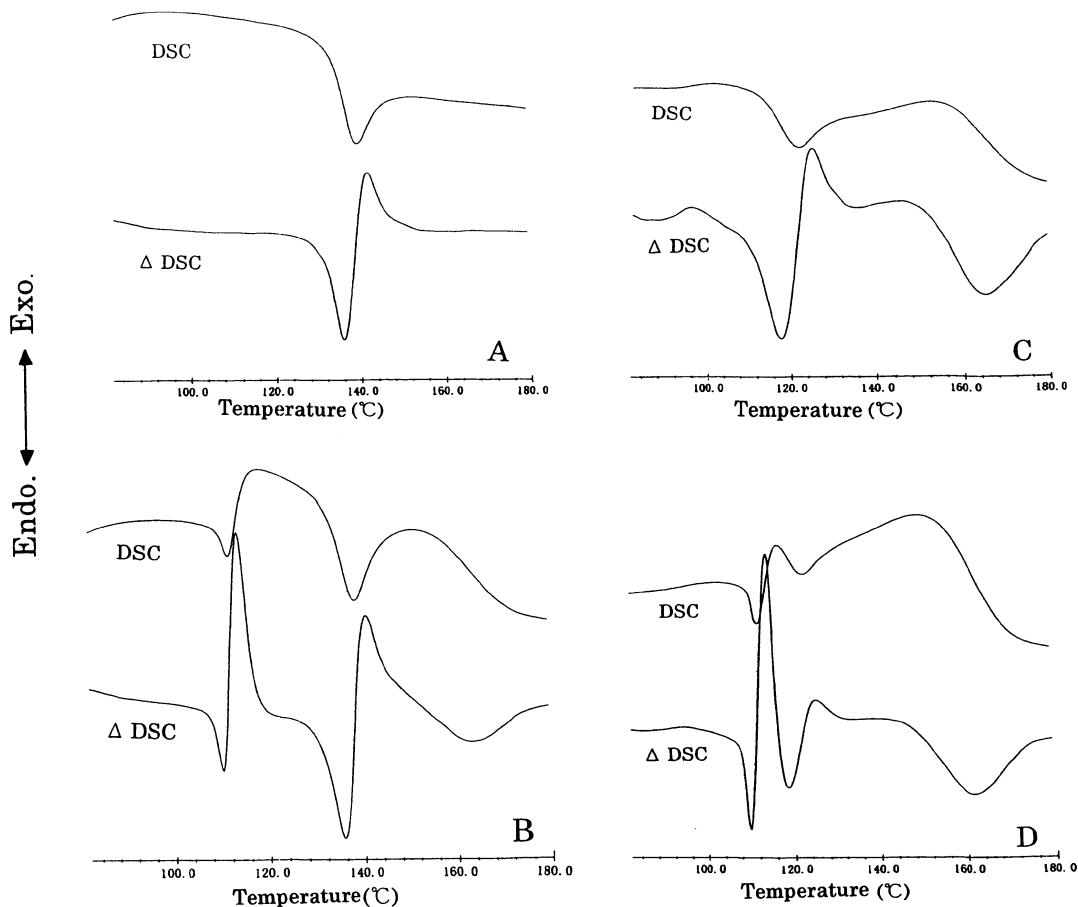


Fig. 3 Changes in DSC patterns before and after the addition of BPO to a BPO-free PMMA (MB-8C) and a dental resin powder (Acron). MB-8C before (A) and after addition of 1 mass% BPO (B) and Acron before (C) and after addition of 2 mass% BPO (D)

BPO mixed with the BPO-free PMMA powder (Fig. 4). Therefore, the amount of BPO outside the PMMA powder can be determined from the peak height of  $\Delta$ DSC. Distinguishing whether BPO exists inside or outside the polymer particles is generally impossible with standard analytical methods, but was possible using DSC. Thus, the present study demonstrates for the first time the unique useability of DSC in the characterization of dental resin powders.

The present findings suggest that (1) commercial dental acrylic resin powders usually include BPO inside the polymer particles; (2) their BPO is residual BPO, remaining unreacted at the time of manufacturing polymer beads by suspension polymerization of the monomer; (3) little BPO is intentionally added to adjust the BPO content of dental resin powders; (4) the residual BPO is utilized as initiator; and therefore (5) the BPO content in the powders is not always fixed, but fluctuates

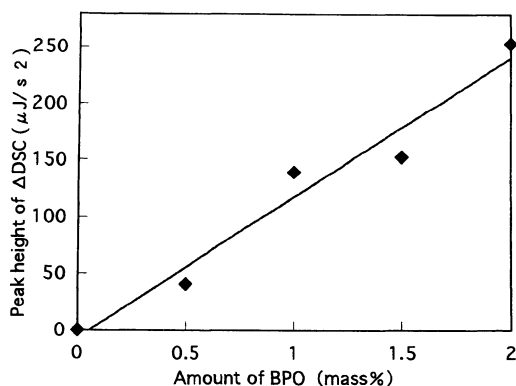


Fig. 4 Correlation between the amount of BPO mixed with a BPO-free PMMA (MB-8C) and the peak height of  $\Delta$ DSC at 114°C.

because the residual BPO varies from batch to batch.

Whether BPO exists inside or outside PMMA particles, it may have a considerable influence on the BPO/amine initiated-polymerization behavior of the resin, consumption of BPO, residual monomers, etc. Regarding these influences, a study is in progress and the results will be reported in the near future.

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