JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 6 (1995) 167–171

Evaluation of the curing behaviour of three commercial VLC inlay composite resins by DSC and DTA thermal analyses

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We examined the curing behaviour by visible-light (VL) and by heat of three commercial VLC inlay composite resins and three commercial VLC direct-filling composite resins by isothermal differential scanning calorimetry (DSC) thermal analysis and DTA thermal analysis, respectively. It became evident that heat of curing with VL irradiation and activation energy for photo-polymerization differed among the composite specimens. The activation energies for VL curing of inlay composites tended to slightly exceed those of direct-filling composites. It also became clear that the activation energy for heat curing of one direct-filling composite was considerably larger than those of the other five composites. There was, however, no systematic difference in the activation energies for heat curing between inlay and direct-filling composites.

1. Introduction

Dental composite resins have been widely accepted as anterior direct-filling materials due to the ease of handling and esthetic merit [1]. They have, however, still not attained general acceptance for use in posterior teeth, particularly for large cavities, mainly because of polymerization shrinkage and wear problems. Polymerization contraction leads to microscopic marginal gaps which may eventually lead to decay. The resin matrix of the composite materials is relatively soft and susceptible to abrasive wear [2–5].

To overcome these problems, the so-called inlay/onlay technique, including extraoral polymerization of the composite resin, has been introduced [6]. The principle is that an inlay is constructed in the patient's mouth with VL, the inlay is then removed from the mouth, and the material is heat-treated to cause further polymerization and crosslinking of the resin. Following the heat treatment, the inlay is cemented permanently (without contraction problem) using a composite resin luting cement [6]. It has been reported that post-curing by heat can cause an increase in hardness and resistance to abrasion [7]. There are, however, few studies, in which the curing behaviour of inlay composites by VL and that by heat are actually examined. One well-accepted technique to evaluate the curing behaviour of dental composites is thermal analysis [8–11].

The purpose of the present study, was, therefore, to investigate the curing behaviour of three commercial VLC inlay composites and three commercial VLC direct-filling composites (as control) by isothermal DSC and DTA thermal analyses, respectively.

2. Materials and methods

2.1. VLC composite resin samples

Table I shows the three commercial VLC inlay composite resins and three commercial VLC direct-filling composite resins examined, with details of type, brand name, batch number, manufacturer, manufacturer's recommended light source and irradiation time for VL curing, and sample code.

2.2. Evaluation of the curing behaviour with VL by DSC thermal analyses

The photopolymerization behaviour of the composite resin specimen was examined by isothermal differential scanning calorimetry (DSC) thermal analysis, using a thermal analyser (DT-30, Shimadzu Co., Kyoto, Japan), while irradiated with VL. The composite specimen (25 mg) held in an aluminum crucible on the DSC cell chamber was photocured by the respective VL source at 15, 37 and 50 °C while maintaining a constant distance of 3.0 mm between the top of the cell and the light source, and the heat released was measured. To obtain the activation energy for polymerization by VL, the peak time required to reach the maximum exotherm and heat of curing were recorded. The heat of curing was determined by calculating the area under the DSC curve for the period 0 to 180 s, and comparing this area with a known heat standard (i.e. the area and heat obtained from the melting of indium). The activation energy for photopolymerization was calculated by the following Arrhenius formula:

$$K = A\exp(-E/RT)$$

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TABLE I List of six commercial VLC composite resins examined, with details of type, brand name, batch number, manufacturer, manufacturer's recommended light source and irradiation time for VL curing, and sample code

Type	Brand name	Batch number	Manufacturer	Light source (irradiation time, s.)	Sample code
Inlay	CR Inlay	1007C	Kuraray Co., Japan	Quick Light (40)	CRI
	Estilux Posterior CVS	Ch.B. 33	Kulzer Co., Germany	Translux EC (40)	CVS
	Brilliant DI	060789 – 19	Coltene Co., Switzerland	Arcus 1 (120)	BDI
Direct-filling	Clear-fil Photo Posterior	1025	Kuraray Co., Japan	Quick Light (30)	CPP
	P-50	9350U	3M Co., U.S.A.	Optilux (30)	P50
	Brilliant Lux	190489-16	Coltene Co., Switzerland	Arcus 1 (60)	BLX

$$\log_{10}K - \log_{10}A = -E/2.3R(1/T)$$

where K is the reaction time (= heat of curing/peak time = H/t_P), R is the gas constant, A is a frequency factor, T is the absolute temperature of the DSC cell chamber, and E is the activation energy for photopolymerization.

Experiments were repeated five times on each specimen.

2.3. Evaluation of the heat curing behaviour by DTA thermal analyses

The thermal change of the composite resin paste upon heating was studied by DTA thermal analysis with a thermal analyser (DT-30, Shimadzu Co., Kyoto, Japan). The experimental DSC conditions were as follows: sample weight = 25 mg; reference material, α-alumina; DTA sensitivity, 100 μV; atmosphere, air under 30 ml/min N_2. The furnace temperature was raised linearly from room temperature to 800 °C at a heating rate of 2, 5 and 10 °C/min. The change in the peak temperature of the first exothermic reactions were monitored. Activation energy for heat polymerization was calculated by the following Ozawa formula:

$$\log_{10}a = \text{constant} - E/2.3R(1/T)$$

where a is the rate of heating, E is the activation energy for VL-curing, R is the gas constant, and T is the absolute peak temperature of the first exotherm.

Experiments were repeated five times on each specimen.

3. Results

Fig. 1 shows the DSC profiles of six composite specimens while being photo-cured at 37 °C. CRI exhibited the shortest time to reach the peak of photopolymerization, followed by CPP, P50, BDI and BLX, while CVS showed the longest. CRI displayed the widest peak height of photopolymerization, followed by CPP, P50, BDI and BLX, whilst CVS showed the narrowest. Table II indicates the heat of curing released at 15, 37 and 50 °C due to photopolymerization of six composite specimens. CRI released the maximum heat, followed by CVS, CPP and BLX, while BDI and P50 showed the least. Fig. 2 shows the effects of three different ambient temperatures on DSC curves of a composite specimen (CRI), while being irradiated with VL. For all composite specimens, increasing the ambient temperature resulted in reduction in the time reaching the peak, and an increase in the peak height. Fig. 3 shows an Arrhenius plot used to determine the activation energy of polymerization by VL of an inlay composite (CRI). For all data, there existed a high linear regression coefficient, r between

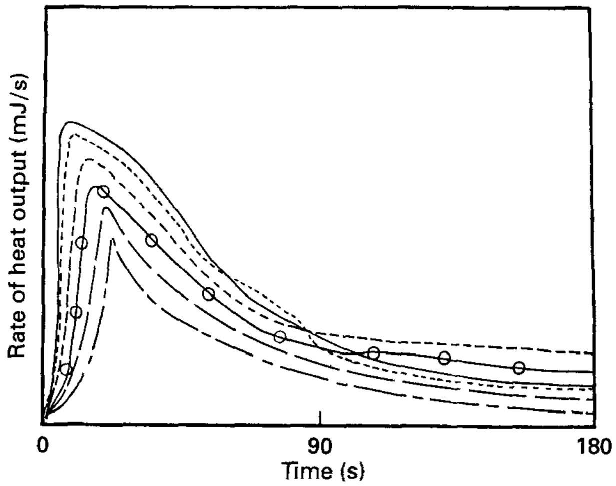

Figure 1 DSC profiles at 37 °C of the six commercial VLC composite resins examined: — CRI; - - - CPP; —— P50; -⊖- BDI; —— BLX; —·— CVS.

TABLE II The heat of curing, determined by isothermal DSC thermal analyses of six commercial VLC composite resin samples, expressed as mean values of five measurements with standard deviations

Temperature	Type	Sample code	Heat of curing (J/g)
15 °C	Inlay	CRI	437.5 ± 22.3
		CVS	185.4 ± 20.9
		BDI	159.4 ± 14.7
	Direct-filling	CPP	204.9 ± 18.3
		P50	151.1 ± 20.2
		BLX	210.9 ± 25.6
37 °C	Inlay	CRI	484.2 ± 18.5
		CVS	255.4 ± 21.2
		BDI	174.3 ± 18.4
	Direct-filling	CPP	248.4 ± 21.2
		P50	178.8 ± 20.4
		BLX	241.2 ± 15.4
50 °C	Inlay	CRI	513.4 ± 42.3
		CVS	294.2 ± 21.5
		BDI	209.2 ± 19.7
	Direct-filling	CPP	263.2 ± 23.1
		P50	191.7 ± 19.4
		BLX	262.1 ± 25.1

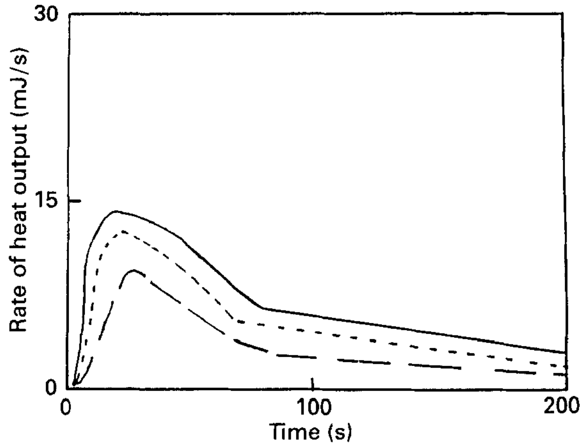

Figure 2 Effects of three different temperatures on the DSC profiles of an inlay composite resin (CRI), while being irradiated by VL: — 50 °C; - - - 37 °C; —— 15 °C.

log (H/t_p) and $1/T$, less than − 0.99. Table III indicates the activation energies for photopolymerization of six composite specimens. P50 possessed the minimum activation energy for VL-curing, followed by BLX, CPP, BDI, CVS and CRI.

Fig. 4 shows the DTA profiles of six composite specimens at a heating rate of 10 °C/min. All DTA curves showed exothermic peaks (i.e. first exothermic reactions) in the range 90–120 °C due to polymerization by heat, and complicated thermal reactions at elevated temperatures of more than 300 °C arising from thermal decomposition of the set composites. CRI had the lowest exothermic temperature, followed by BDI, CVS, P50, BLX and CPP. Fig. 5 indicates the effect of heating rate on the exothermic peaks of a composite specimen (CRI). For all composite specimens, increase in heating rate brought about a decrease in the peak temperature. Fig. 6 shows an Ozawa plot used to determine the activation energy of polymerization by heating of an inlay composite (CRI). For all data, there existed a high r between log a and $1/T$, less than − 0.99. Table IV shows the activation energies for heat polymerization of six composite specimens. BDI had the least activation energy for heat polymerization, followed by CVS, BLX, P50, CRI and CPP.

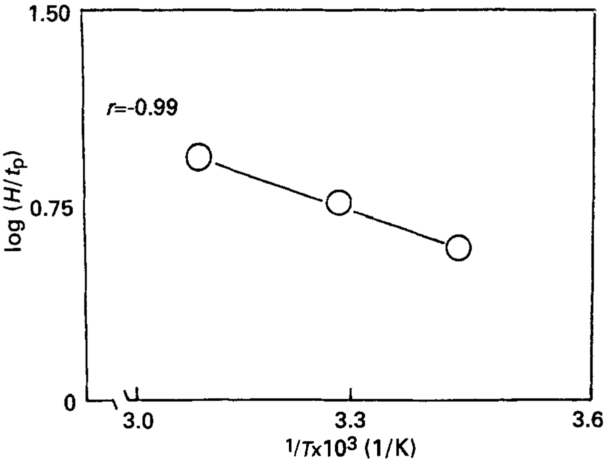

Figure 3 An Arrhenius' plot used to determine the activation energy of polymerization by VL of an inlay composite (CRI).

TABLE III Activation energies for polymerization by VL of six VLC composite resins (kcal/mol), expressed as mean values of five measurements with standard deviations

Type	Sample code	Activation energy for polymerization by VL (kcal/mol)
Inlay	CRI	3.22 ± 0.12
	CVS	3.13 ± 0.23
	BDI	2.91 ± 0.15
Direct-filling	CPP	2.52 ± 0.22
	P50	1.51 ± 0.19
	BLX	2.05 ± 0.28

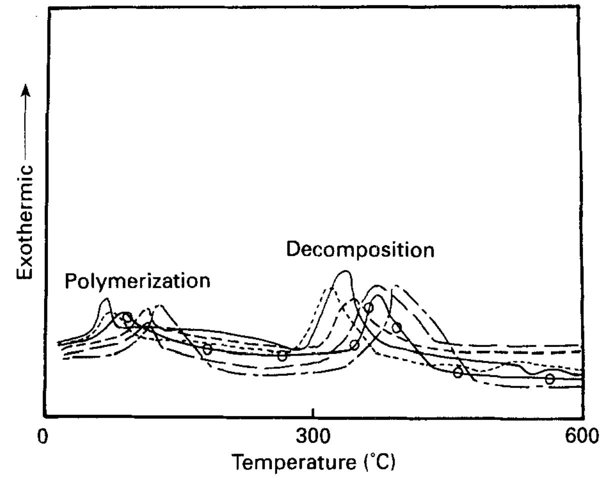

Figure 4 DTA profiles at 10 °C/min of the six commercial VLC composite resins examined: —— CRI; - - - - BDI, – – – CVS; -⊖- P50; —— BLX; —·— CPP.

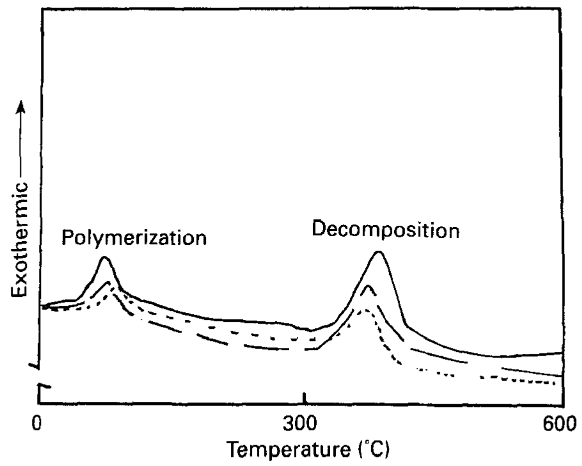

Figure 5 Effects of three different heating rates on the DTA profiles of an inlay composite resin (CRI): —— 10 °C/min; — — 5 °C/min; --- 2 °C/min.

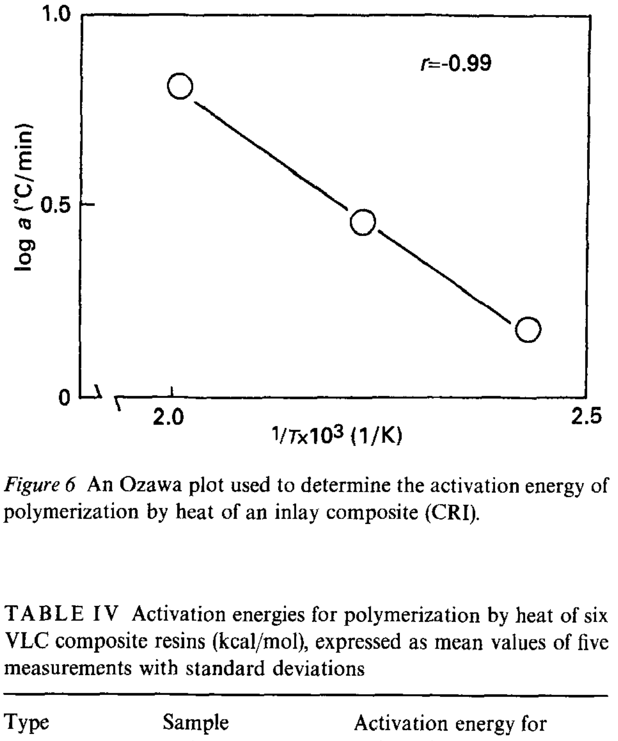

Figure 6 An Ozawa plot used to determine the activation energy of polymerization by heat of an inlay composite (CRI).

TABLE IV Activation energies for polymerization by heat of six VLC composite resins (kcal/mol), expressed as mean values of five measurements with standard deviations

Type	Sample code	Activation energy for polymerization by heat (kcal/mol)
Inlay	CRI	37.41 ± 1.32
	CVS	25.83 ± 0.94
	BDI	20.25 ± 1.22
Direct-filling	CPP	76.34 ± 3.14
	P50	28.72 ± 2.23
	BLX	25.39 ± 2.98

4. Discussion

In isothermal DSC analyses, composite resin samples were exposed to VL irradiation to obtain the heat of curing and activation energies. In this study, each composite specimen was photocured by the respective manufacturers' recommended light sources to evaluate the clinical performance of each composite sample. Upon VL irradiation, radicals formed upon the C =C double bonds of the multifunctional monomers, liberating heat. Thus, heat of curing is a function of monomer conversion. It is judged that the more heat is released, the greater the conversion of monomers. It was observed that CRI exhibited a larger heat of curing than the other five composite specimens. This might be attributed to the presence of active four-functional monomers in CRI. Without the exact monomer formulations, however, it is not possible to estimate the degree of conversion of each composite specimen. The degree of monomer conversion of the composite specimens has been evaluated by FTIR (Fourier transformed infrared spectroscopy) [12–14]. Here, the activation energy provides the scale to assess the ease of VL-curing of composite specimens. In general, activation energy governs the rate of chemical reaction [15]. The lower the activation energy, the easier it is to process the chemical reaction (e.g. monomer conversion). The activation energies for photopolymerization of inlay composites (e.g. CRI) were slightly larger than those of direct-filling composites (e.g. P50). This may be due to the concentration of initiator and inhibitor [16], and the level of light transmittance through the composite paste [17]. It can be speculated that to facilitate a similar level of photocuring, more energy is required for inlay composites than for direct-filling composites.

In DTA thermal analyses, photocurable composite specimens were polymerized by heat. Since post-curing by heat is recommended for VLC inlay composites (e.g. CRI), these experiments were conducted to assess the efficiency of heat in curing these composites. When heated, CQ can be transformed into radicals, converting monomers, or monomers can be directly converted without the aid of free radicals. These two factors may simultaneously act, generating the first exothermic reaction of each composite specimen. The activation energy for heat of a direct-filling composite (CPP) was considerably larger than those of the other five composites. The reason for this might stem from the incorporation of monomers which were less reactive to heat curing. No clear differentiation was found in the activation energy for heat polymerization between inlay and direct-filling composite specimens. It is assumed that to achieve the equivalent level of heat curing, more energy is needed to heat-cure CPP than when curing the other five samples.

5. Conclusions

We examined three commercial VLC inlay composite resins and three commercial VLC direct-filling composite resins for their curing behaviour by VL and by heat, using isothermal DSC and DTA thermal analyses, respectively. The following findings were obtained.

(1) It was suggested from the measurements of activation energies for VL curing that greater energies were required for inlay composites than for direct-filling composites to achieve a similar level of curing.

(2) It became evident from the measurements of activation energies for heat curing that more energy was needed to cure one direct-filling composite (CPP), than that needed to cure the other five composites.

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Received 10 September 1993
and accepted 27 April 1994