JOURNAL OF MATERIALS SCIENCE 22 (1987) 1295–1298

Thermoanalytical evaluation of visible-light-cured composites

H. SHINTANI, K. WAKASA*, M. YAMAKI*
*Department of Operative Dentistry, and *Department of Dental Materials, Hiroshima University, School of Dentistry, Hiroshima 734, Japan*

Kinetic analysis of thermogravimetric data in visible-light-cured composite restoratives has been carried out and a comparison was made with that for a conventional chemically-cured composite. The results reveal that the thermal decomposition of polymers as the base resin in the composites may be governed by a single process, and the value of activation energy is different in decomposing the base resins thermally. The different values suggest that the kinds of base resins and the catalysts may have an effect on the thermal decomposition.

1. Introduction

Recently, visible-light-cured composite resins have been widely used in the field of clinical dentistry as aesthetic restorative materials. This type has advantages in comparison with the paste–paste type, such as less porosity and longer working time [1, 2]. Furthermore, the physico-chemical properties of visible-light-cured composite resins are superior to those of conventional chemically-cured composite resins [3]. However, little is known about this thermal behaviour of the composites [4].

The present study was designed to clarify the thermal behaviour of visible-light-cured composites and to obtain the activation energy for thermal decomposition by thermogravimetric (TG) analysis using a thermal analyser.

2. Materials and methods

Three visible-light-cured composite resins (A, B and C) and one chemically-cured composite resin (D) were tested. Codes, product names, batch numbers, supplier and light unit are listed in Table I. Sample resins were cured according to manufacturers' instructions in a cylindrical mould (6.84 mm diameter and 1.42 mm height). After curing, they were taken out and then crushed mechanically using a mortar. Powders thus prepared were sieved to obtain those particle sizes of less than 100 mesh, 10 mg of which were then subjected to differential thermal analysis (DTA) and thermogravimetry (TG) using thermal analysis equipment (Shimadzu DT-30, Shimadzu Co, Kyoto, Japan). DTA was carried out under a constant air flow of 50 ml min^{-1} and with varying heating rates 2, 5 and 10° C min^{-1} in the temperature range 30 to 900° C (these heating rates are those which are set on the equipment, but the real heating rates which are measured automatically have slightly higher values).

The measured sensitivity ranges of DTA and TG were, respectively, 200 μV and 20 mg (the temperature was measured using a Pt-to-(Pt + 13 wt % Rh) thermocouple). Five samples from each formulation were tested. The peak temperatures of the composites were obtained from a DTA curve, while their activation energies were calculated according to the equations given in the Appendix.

TABLE I Composite products used in this study

Code	Product name	Batch no.	Manufacturer	Light unit
A	Silux	081784	3M Co. St Paul, Minnesota	Optilux (Demetron Co.)
B	Lite-Fil A	018531	Shofu Inc. Kyoto, Japan	Daylight Lamp (Shofu Inc.)
C	Photo Clearfil A	11111A	Kuraray Co. Osaka, Japan	Quicklight (J. Morita Co.)
D	Clearfil Posterior	11111	Kuraray Co. Osaka, Japan	

A, B, C, visible-light-cured composite resin; shade, universal.
D, chemically-cured composite resin.

3. Results and discussion

Thermal analysis of four composite restoratives listed in Table I was carried out over the temperature range 30 to 900° C. The results are given in Fig. 1 as the TG curves depending on a heating rate of 2° C min^{-1}. Two points were noted in the TG curves. Firstly, for all four composite restoratives, there was a large weight loss in the temperature range 200 to 450° C. The largest weight loss occurred in A, one of the visible-light-cured composites. Secondly, there was little weight loss in the higher temperature range 600 to 900° C. From Table II the average filler contents,

TABLE II Filler contents of various composite resins (% wt/wt) (heating rate 10° C min^{-1})

Temp. (° C)	Composite resin code			
	A	B	C	D
600	56.88	83.32	86.72	82.20
700	56.56	83.76	86.89	80.61
800	56.52	83.79	87.06	79.46
900	56.42	83.83	86.98	79.00
*	51	84	84	78

*Information supplied by the manufacturers.

0022–2461/87 $03.00 + .12

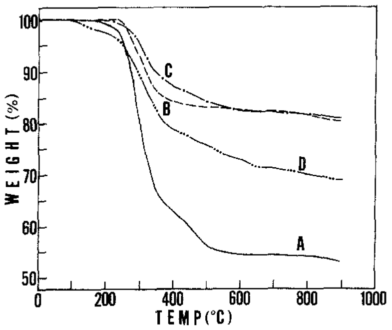

Figure 1 Thermogravimetric (TG) curves of composite resins, A, B, C (visible-light-cured composite resins) and D (chemically-cured composite resins) at a heating rate of 2° C min^{-1}.

obtained from weight loss in thermal analysis, were A (56% wt/wt), B (83% wt/wt), C (87% wt/wt) and D (80% wt/wt). The filler contents of composite resins based on the ISO specification [5], that is, at 600° C, were 56.88 (A), 83.32 (B), 86.72 (C) and 82.20 (D). These results were similar to those described by the manufacturers (Table II). The weight loss of composite resins is dependent on the thermal decomposition of the cross-linked polymer [4], because the fillers within the composite resins are not decomposed thermally. From the nature of the TG curves it was deduced that thermal decomposition occurred by chain scission [4].

Figs 2a to d show the TG and DTA curves of composite resins A, B, C and D at heating rates of 2, 5 and 10° C min^{-1}. The shapes of the TG curves were essentially the same at all heating rates over the entire temperature range of the composite resins. The TG curves changed progressively to higher temperatures with increasing heating rates. On the other hand, the DTA curves of visible-light-cured resins (A, B and C) had the same exothermic peak as a chemically-cured resin D. The main peaks of exothermic reaction were found near the end of the decrease in the thermogravimetry, that is, the thermal decomposition. The results, presented in Table III, demonstrate that the main exothermic peak temperatures were found in the test temperature range of 200 to 450° C. The peak temperatures changed to higher values with an increase in heating rate of 2 to 10° C min^{-1}. The changes for A (352.9 to 388.2° C), B (327.5 to 356.9° C) and C (319.2 to 365.4° C) were lower than that for D, the chemically-cured composite (373.1 to 435.3° C).

TABLE III Exothermic peak temperature of the composites (° C)

Heating rate (° C min^{-1})	Composite resin code			
	A	B	C	D
2	352.9	327.5	319.2	373.1
5	364.7	356.9	359.6	386.5
10	388.2	356.9	365.4	435.3

In Fig. 3, log heating rate is plotted against the inverse of the absolute temperature at a given weight loss in the range 1 to 15%. The plots are linear at each weight loss of the composite resin, indicating that here thermal decomposition is governed by a single process. The activation energy was thus calculated according to Equation A7 in the Appendix. In Table IV a to d, the activation energy in given for weight losses in the composites A to D, respectively is indicated.

The results in Table IV are: (1) the activation energy of the visible-light-cured composites, A and B, showed high values of 54.18 ± 3.83 and 65.03 ± 10.75 kcal mol^{-1}, respectively, but the activation energy of composite C was 23.39 ± 1.96 kcal mol^{-1}; and (2) the activation energy in the chemically-cured composite (D) was 15.08 ± 0.47 kcal mol^{-1}. In general, the type of base resin and the amount of

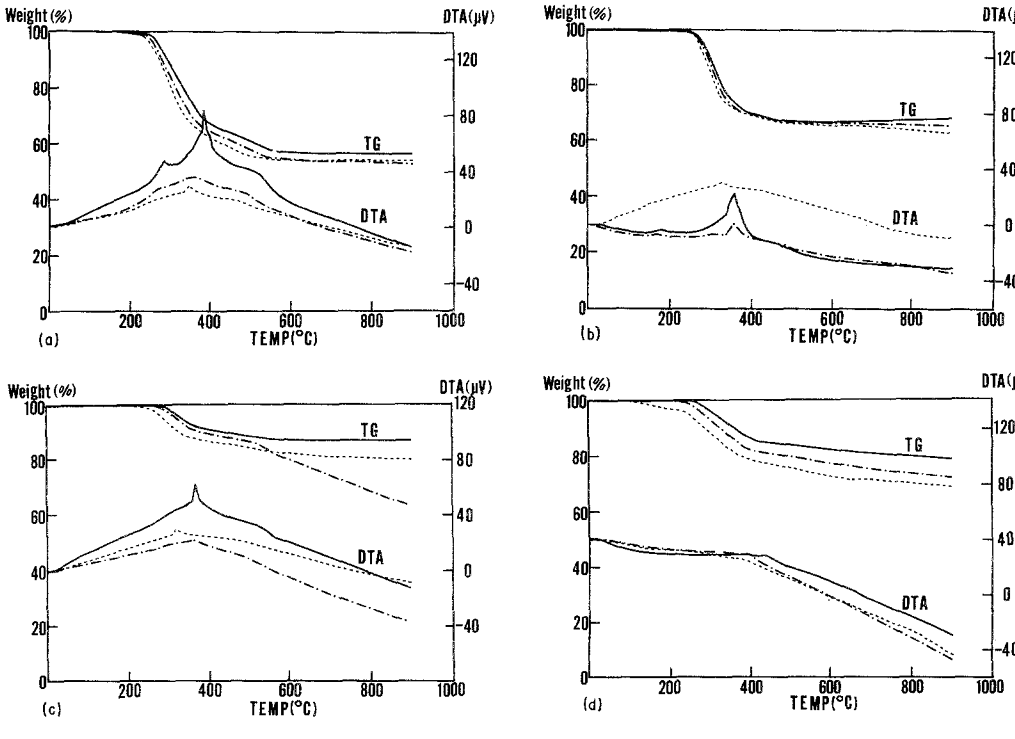

Figure 2 Thermogravimetric (TG) and differential thermal analysis (DTA) curves of composite resins: (a) A, (b) B, (c) C and (d) D at heating rates of (----) 2° C min^{-1}, (-·-) 5° C min^{-1} and (——) 10° C min^{-1}

TABLE IV (a) to (d) Activation energy at each weight loss in the composites A to D

(a) A

Weight loss (%)	Activation energy ($\mathrm{kcal\,mol^{-1}}$)
5	51.41
6	56.18
7	53.93
8	51.46
9	52.03
10	59.67
11	57.50
12	59.74
13	54.59
14	52.21
15	47.31
mean ± S.D.	54.18 ± 3.83

(b) B

Weight loss (%)	Activation energy ($\mathrm{kcal\,mol^{-1}}$)
1	82.32
3	63.76
5	58.31
7	54.75
11	66.11
13	61.19
15	79.85
mean ± S.D.	65.03 ± 10.75

(c) C

Weight loss (%)	Activation energy ($\mathrm{kcal\,mol^{-1}}$)
3	25.21
4	24.39
5	25.26
6	23.13
7	22.05
8	20.29
mean ± S.D.	23.39 ± 1.96

(d) D

Weight loss (%)	Activation energy ($\mathrm{kcal\,mol^{-1}}$)
5	14.87
6	15.47
7	15.76
8	15.74
9	15.28
11	14.88
12	14.59
13	15.11
14	14.66
15	14.43
mean ± S.D.	15.08 ± 0.47

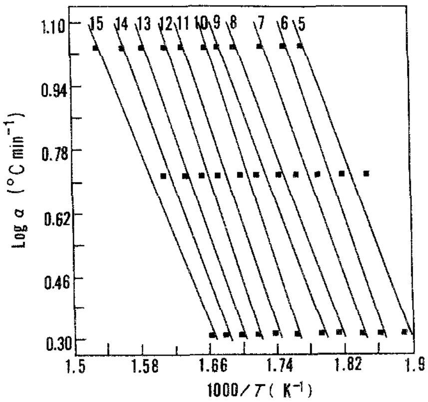

Figure 3 Typical plots of the reciprocal absolute temperature against the logarithm of the heating rate for various weight losses of 1 to 15% in a visible-light-cured composite resin A. The real heating rates changed a little after setting them at 2, 5 and 10° C min^{-1}, and the new rates were used to calculate the activation energy.

camphorquinone used as catalyst are different in commercial visible-light-cured composite [6], the benzoyl peroxide (BPO) (a chemical catalyst) is included in the chemically-cured composite, D. Thus base resins are composed of such multi-functional monomers as bisphenol-A diglycidyl methacrylate (bis- GMA) and triethylene glycol dimethacrylate (3G) [6, 7], but the quantitative amounts are different between the composites. It is suggested that the values of activation energy are different when the base resins are thermally decomposed. Thus we tried to examine how the activation energy varies with quantitative changes of base resin and catalyst.

Appendix

The thermoanalytical data of a resin can be determined by kinetic analysis, because the thermal behaviour in a thermal decomposition process is governed by a specific reaction rate. As composite materials comprise a resin matrix and a filler, the thermal behaviour may be described as follows: the rate constant, k, is assumed to be governed by

$$k = A \exp(-\Delta E/RT) \qquad \text{(A1)}$$

where A, ΔE, R and T are the frequency factor, the activation energy, the gas constant and the absolute temperature, respectively [8]. The rate expression for the disappearance of reactant from such a mixture as the resin material is

$$-(\mathrm{d}x/\mathrm{d}t) = kx^n \qquad \text{(A2)}$$

where x and n are the fraction of reactant of resin matrix and the order of reaction, respectively. Using Equations (A1) and (A2),

$$-(\mathrm{d}x/\mathrm{d}t) = A \exp(-\Delta E/RT)\, x^n \qquad \text{(A3)}$$

[8–12].

Thermogravimetric analysis measures the weight loss of the resin material when it is heated to a desired temperature. In this analysis, kinetic thermal parameters at a constant heating rate are obtained from the thermogravimetric results. This method can be applied to all types of phenomenon with a single activation energy. Thus, it can be applied to thermoanalytical curves of a first-order reaction ($n = 1$) and the activation energy for the thermal first-order decomposition reaction, $-(\mathrm{d}x/\mathrm{d}t)$, can be calculated.

As x changes with increasing temperature (x is expressed as a function $f(x)$ when x changes according to the reaction with a first order, $n = 1$)

$$-\int_{x_0}^{x} \mathrm{d}x/f(x) = (A/a)\int_{T_0}^{T} \exp(-\Delta E/RT)\,\mathrm{d}T \quad \text{(A4)}$$

where T_0 is T at $t = t_0$. As the rate of the reaction is very low at T_0 [11], the next approximation for the right-hand side of Equation A4 is expressed and tabulated as

$$\int_{T_0}^{T} \exp(-\Delta E/RT)\,\mathrm{d}T = \int_{0}^{T} \exp(-\Delta E/RT)\,\mathrm{d}T$$
$$= (\Delta E/R)P[\Delta E/RT] \quad \text{(A5)}$$

The left-hand side of Equation A4 is constant, because it is a function depending on only the fraction x.

If the weight decreases at temperature T_1 for a heating rate a_1, at T_2 for a_2, and at T_3 for a_3,

$$(A\Delta E/a_1 R)P[\Delta E/RT_1] = (A\Delta E/a_2 R)P[\Delta E/RT_2]$$
$$= (A\Delta E/a_3 R)P[\Delta E/RT_3] \quad \text{(A6)}$$

where $\log P[\Delta E/RT] \approx -2.315 - 0.4567(\Delta E/RT)$ [11].

Using the p-function, the following linear relations are written [10]:

$$-\log a_1 - 0.4567(\Delta E/RT_1)$$
$$= -\log a_2 - 0.4567(\Delta E/RT_2)$$
$$= -\log a_3 - 0.4567(\Delta E/RT_3) \quad \text{(A7)}$$

Thus, the plots of the logarithm of heating rate against the inverse of the absolute temperature were obtained for a given weight-loss. That is, the activation energy can be estimated by plotting the inverse of the absolute temperature at the peak of the derivative thermoanalytical curve against the logarithm of the heating rate.

References

1. J. W. REINHARDT, G. E. DENEHY, R. D. JORDON and B. R. J. RITTMAN, *Operative Dentistry* **7** (1982) 82.
2. F. LUTZ, J. C. SETCOS, R. W. PHILLIPS and J. F. ROULET, *Dent. Clin. North. Amer.* **4** (1983) 697.
3. C. N. RAPTIS, P. L. FAN and J. M. POWERS, *J. Amer. Dent. Assoc.* **99** (1979) 631.
4. A. ACHARYA and E. H. GREENER, *J. Dent. Res.* **51** (1972) 1363.
5. ISO specification 4049, 1985.
6. H. SHINTANI, T. INOUE and M. YAMAKI, *Dent. Mater.* **1** (1985) 124.
7. R. L. BOWEN, *J. Amer. Dent. Assoc.* **49** (1980) 810.
8. E. S. FREEMAN and B. CARROL, *J. Phys. Chem.* **62** (1958) 394.
9. A. W. COATS and J. P. REDFERN, *Nature* **201** (1964) 68.
10. C. D. DOYLE, *ibid.* **207** (1965) 290.
11. T. OZAWA, *Bull. Chem. Soc. Jpn.* **38** (1965) 1881.
12. T. OZAWA, *J. Thermal Anal.* **22** (1970) 301.

Received 6 February
and accepted 5 August 1986