

# Setting time of composite restorative resins vs. content of amine, peroxide, and inhibitor

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The setting time was measured for a number of experimental composite resin formulations with varying content of amine, peroxide, and inhibitor. Assuming a bimolecular reaction between amine and peroxide and on the basis of reaction kinetics, an equation was obtained expressing setting time in terms of content of amine, peroxide, and inhibitor. The experimental data were found to fit the equation at a high level of statistical significance ( $p < 0.001$ ).

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The polymerization of chemically activated restorative resins is usually initiated through a reaction between benzoyl-peroxide and a tertiary amine. To provide for sufficient working time the setting is delayed by the addition of suitable amounts of a phenolic inhibitor. The accelerating effect of various amines has previously been investigated (1, 4, 5). Further, the influence on gel time of the amine/peroxide ratio has been studied (2). However, the combined effect on setting time of amine, peroxide, and inhibitor has not been described in the dental literature.

It was the purpose of the present work 1) on a composite resin formulation to study the relationship between setting time and content of amine, peroxide, and inhibitor; and 2) to analyze the relationship on the basis of reaction kinetics.

## MATERIALS AND METHODS

The setting time was measured using a number of experimental pastes containing either amine or peroxide. Except for the content of inhibitor, amine and peroxide, these pastes were of identical composition: a monomer consisting of 50 mole % BISGMA and 50 mole % TEGDMA (triethylene-glycol-dimethacrylate), in which a silanized, conventional filler was dispersed. The filler content was 75.0 percent by weight. As regards inhibitor, amine, and peroxide varying amounts of MHQ (hydroquinone-monomethyl-ether) and either DEPT (N, N-diethanol-p-toluidine) or BPO (benzoyl-peroxide) were dissolved in the monomer of each paste. The monomer content of MHQ, DEPT and BPO will be specified under results.

Equal amounts ( $0.1 \pm 0.005$  g) of an

amine-containing paste and a peroxide-containing paste were mixed for 25 seconds, and the setting time was determined as described for «working-time» in the American Dental Association Specification No. 27 for direct filling resins (9), except that the time was recorded to the nearest 10 seconds. For each combination of pastes the measurement of setting time was carried out in duplicate and the mean value recorded.

### RESULTS

The results are presented in Table 1. The content of amine and peroxide is given in weight per cent of the monomer of the unmixed pastes (the peroxide used contained 20% water, the weight of which for practical reasons is included in the content of peroxide stated in the table). The added inhibitor is given in weight per thousand of the monomer in the pastes (before and after mixing).

As could be expected the setting time was found to increase with content of inhibitor and to decrease with content of amine and peroxide.

Each setting time given is the mean of two determinations. The differences between the two measurements, expressed in per cent of the mean value, averaged about 6%.

### DISCUSSION

A relationship between setting time and content of amine, peroxide and inhibitor was derived as follows: A bimolecular reaction between amine and peroxide, whereby free radicals are produced, is assumed. These radicals may 1) react with the monomer to initiate polymerization or 2) react with the inhibitor and become inactive with re-

spect to the polymerization process (3). The inhibitor in the system may 1) react with the above mentioned radicals or 2) react with the peroxy-radicals formed by the facile addition of dissolved oxygen to the initiated monomer (or polymer) radical (6). Oxygen alone also has an inhibitory effect by combining with the initiated monomer radical (6). If the initial concentrations of amine and peroxide in the monomer of a mixture of pastes are called  $a$  and  $b$ , respectively, and these quantities are reduced by the amount  $x$  at the time  $t$ , the following equation applies (8)

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt \quad (I)$$

in which  $k$  is a constant.

If the material sets at a time  $t_s$  at which  $x = x_s$  is small compared to  $a$  and  $b$ , the above equation reduces to

$$\frac{x_s}{a \cdot b} = k \cdot t_s \quad (II)$$

It may be assumed that the quantity,  $x_1$ , of peroxide having reacted at the end of the inhibition period is approximately given by

$$x_1 = \alpha \cdot o + \beta (i_o + i)$$

where  $\alpha$  and  $\beta$  are constants,  $o$  is the initial oxygen concentration,  $i_o$  the concentration of inhibitor present in the monomer when received from the supplier, and  $i$  the concentration of admixed inhibitor.

The quantity,  $x_s$ , of peroxide having reacted at the time of setting is

$$x_s = x_1 + x_2 = \alpha \cdot o + \beta (i_o + i) + x_2 \quad (III)$$

where  $x_2$  is the quantity of peroxide reacting after the end of the inhibition period until setting of the material. For

Table 1. Setting time vs. content of amine (DEPT), peroxide (BPO), and inhibitor (MHQ)

DEPT (%)*	BPO (%)*	MHQ (‰)*	Setting time (min)
0.5	0.5	0	5.6
0.5	1.0	0	2.5
0.5	2.0	0	1.4
1.0	0.25	0	6.9
1.0	0.5	0	2.9
1.0	0.5	0.17	6.3
1.0	0.5	0.33	12.5
1.0	1.0	0	1.5
1.0	2.0	0	0.8
1.5	0.25	0	5.8
1.5	0.5	0	2.2
1.5	0.5	0.17	4.8
1.5	0.5	0.33	9.5
1.5	1.0	0	1.0
2.0	0.25	0	4.4
2.0	0.5	0	1.8
2.0	0.5	0.17	4.8
2.0	0.5	0.33	5.8
2.0	0.5	0.50	13.4
2.0	0.5	0.66	11.3
2.0	0.5	1.0	18.4
2.0	1.0	0	0.9
2.0	1.0	0.33	2.7
2.0	1.0	0.50	3.6
2.0	2.0	0.33	1.4
2.0	2.0	0.50	1.7
2.5	0.25	0	4.2
2.5	0.5	0	1.7
2.5	0.5	0.33	6.0
2.5	0.5	0.50	10.0
3.0	0.25	0	3.3
3.0	0.5	0	1.4
3.0	0.5	0.33	4.8
3.0	0.5	0.50	8.0

\*) The content of amine and peroxide is given in weight per cent of the monomer in the unmixed pastes (The BPO contained 20 % of water, which is included in the values stated). The added amount of inhibitor is given in weight per thousand of the monomer in both of the pastes.

a given monomer  $o$ ,  $i_0$  and  $x_2$  can be assumed to be constant.

Using this expression for  $x$ , the above equation (II) becomes

$$t_s = \frac{1}{k} \frac{\alpha \cdot o + \beta \cdot i_0 + x_2}{a \cdot b} + \frac{\beta}{k} \frac{i}{a \cdot b} \tag{IV}$$

It thus appears that the setting time  $t_s$  may be expressed in terms of two variables:

$$z_1 = \frac{1}{a \cdot b} \text{ and } z_2 = \frac{i}{a \cdot b}$$

Using these variables three-dimensional regression analysis was carried out (7). Obviously, for this purpose  $a$ ,  $b$  and  $i$  may be expressed in any desired measure of concentration. The setting times and concentrations given in Table 1 were used in the analysis. The regression equation found is

$$t_s = 0.2 + 1.5 \frac{1}{a \cdot b} + 16 \frac{i}{a \cdot b}$$

This equation «explains» 92 % of the total observed variation. The standard errors of the regression coefficients are 0.24 and 0.86, respectively. The regression coefficients differ from zero at the  $p = 0.001$  level, whereas the constant term does not differ significantly from zero. These results thus support the above made assumptions.

In conclusion it has been shown that on the basis of reaction kinetics a simple equation can be set up that, within the concentration limits of this study, links setting time of a restorative resin with content of amine, peroxide, and inhibitor. Other molecular species of monomer, amine etc. may change the parameters of the equation, but its general form will remain unchanged.

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