Hardness of restorative resins: effect of camphorquinone, amine, and inhibitor

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The influence of the content of camphorquinone (CQ), amine (DABE), and inhibitor (MHQ) on the Wallace indentation hardness of light-curing polymers was investigated. The hardness was measured on disc-shaped specimens made from 50 bisphenol-A-glycidyl-dimethacrylate/ triethyleneglycol-dimethacrylate-based monomers with various contents of CQ, DABE, and MHQ. When no MHQ had been added, the hardness number decreased with increasing content of CQ. This was also the case with increasing content of DABE, but to a lesser extent. In the presence of MHQ, the contents of CQ and DABE did not influence the hardness number significantly. □ *Dental materials; polymerization catalysts; restorative dentistry*

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It is desirable for a restorative resin to be able to resist abrasion. It has been hypothesized that the Wallace indentation hardness of smooth surface resins—that is, microfilled and unfilled resins—is a predictor of the abrasion resistance (1). With regard to rough surface resins, the indentation hardness of the polymer between the macrofiller particles is supposed to be a governing property.

Several factors have been found to influence the hardness of restorative resins of the chemically curing type: inhibitor content (2), degree of conversion of double bonds (2, 3), content and type of monomer (4, 5), and content and type of initiator (2). However, only little information can be found in the literature regarding the hardness of light-curing polymers in relation to composition (2).

It was the aim of the present study to investigate the influence of the content of camphorquinone, amine, and inhibitor in the monomer mixture on the Wallace indentation hardness of restorative resin-based polymers.

Materials and methods

The Wallace indentation hardness was measured on several light-cured polymers with different compositions. The monomer mixture consisted of 50 weight % bisphenol-A-glycidyl-dimethacrylate (BISGMA) and 50 weight % triethyleneglycol-dimethacrylate (TEGDMA). The monomer content of the amine para-*N*,*N*-dimethylaminobenzoic acid ethyl ester (DABE) was 0.1%, 0.2%, 0.3%, 0.4%, or 0.5% by weight. Likewise, the monomer content of the initiator camphorquinone (CQ) was 0.1%, 0.2%, 0.3%, 0.4%, or 0.5% by weight. In one part of the investigation 0.025 weight % hydroquinone-monomethyl ether (MHQ) was added as extra inhibitor, whereas in the other part no extra inhibitor was added. After addition of DABE, CQ, and MHQ to the monomers, the mixtures were stirred in a dark room until dissolved.

The 50 monomer mixtures were used to produce disc-shaped test specimens. Monomer was pipetted into a cylindrical brass mold (diameter, 10 mm; height, 1 mm) and cured between two pieces of transparent plastic film with a visible-light curing unit (Translux, Kulzer & Co., FRG) for 40 sec on each side. The specimens were placed at 37°C for 24 h before being ground flat on both sides on no. 1000 carborundum paper. The hardness was then measured at five dif-

Table 1. Wallace hardness (μm) in relation to monomer content of camphorquinone and amine. The amine was para-*N*,*N*-dimethylaminobenzoic acid ethyl ester. No extra inhibitor was added to the monomer

	Camphorquinone				
Amine	0.1%	0.2%	0.3%	0.4%	0.5%
0.1%	29.2 ± 1.6	22.0 ± 2.2	23.0 ± 2.3	21.5 ± 2.4	20.0 ± 2.4
0.2%	24.6 ± 4.3	24.1 ± 3.0	20.7 ± 2.1	20.5 ± 3.1	23.4 ± 2.7
0.3%	24.3 ± 2.6	22.5 ± 2.4	19.1 ± 2.1	20.9 ± 1.8	21.7 ± 1.4
0.4%	23.7 ± 3.6	22.4 ± 3.9	21.2 ± 1.2	19.9 ± 1.8	20.0 ± 1.3
0.5%	24.2 ± 5.7	22.3 ± 2.8	20.3 ± 2.4	19.5 ± 1.4	19.2 ± 2.4

Table 2. Wallace hardness (μm) in relation to monomer content of camphorquinone and amine. The amine was para-*N*,*N*-dimethylaminobenzoic acid ethyl ester. The monomer contained 0.025% hydroquinone-monomethyl ether

	Camphorquinone				
Amine	0.1%	0.2%	0.3%	0.4%	0.5%
0.1%	28.2 ± 2.4	20.2 ± 1.6	20.1 ± 3.0	21.3 ± 4.3	20.6 ± 1.7
0.2%	20.7 ± 2.6	20.1 ± 2.1	20.6 ± 2.6	19.5 ± 1.4	18.9 ± 1.6
0.3%	19.0 ± 2.2	22.5 ± 2.4	21.4 ± 2.2	21.2 ± 3.7	18.8 ± 2.1
0.4%	21.0 ± 2.6	23.7 ± 1.9	22.2 ± 2.1	19.7 ± 2.5	23.0 ± 2.7
0.5%	22.4 ± 3.7	22.2 ± 2.1	22.1 ± 2.1	19.8 ± 2.0	20.8 ± 2.3

ferent sites on each specimen, and the mean value was calculated. For each type of polymer the hardness was taken as the mean value obtained from three specimens ($n = 3$). The method of measuring the indentation hardness has earlier been described in greater detail (1). It may be worth mentioning that a higher hardness indentation number indicates a softer material.

Results

The hardness values and standard deviations obtained are shown in Tables 1 and 2 in relation to monomer content of CQ and amine. In Table 1 no extra inhibitor had been added, whereas in Table 2 the monomer mixture contained 0.025% MHQ. The pooled standard deviation for the values in Tables 1 and 2 was 2.6. This implies that each of the recorded values was accurate within ±3.0 μm at a 95% confidence level (6).

Analysis of variance was performed on the hardness numbers in Table 1, and a significant difference between the values was found ($p < 0.025$). The analysis of variance was supplemented with a Scheffé test (7), which showed no difference between the groups with CQ = 0.1% and 0.2%, nor between the groups with CQ = 0.2%, 0.3%, 0.4%, and 0.5% ($p = 0.5$). Likewise, no difference could be detected between the five groups with different content of DABE.

In accordance with earlier work (2), in which the influence of benzoyl peroxide and amine on hardness of chemically curing resins was analyzed, the Wallace hardness was equal to

$$H_W = a \cdot e^{b_1/x_1} \cdot e^{b_2/x_2}$$

In this expression a, b_1, and b_2 are constants, and x_1 and x_2 denote the content of CQ and DABE, respectively. After the equation had been transformed to a linear relationship, regression analysis gave $a = 18.6$, $b_1 = 0.026$, and $b_2 = 0.011$. Both regression coefficients were significantly different from zero ($p < 0.01$). The 'explained' variation corresponds to a coefficient of correlation of $R = 0.85$.

The values in Table 2 were also subjected to analysis of variance, showing $p < 0.05$. However, when the value at CQ = DABE =

0.1% was excluded, the rest of the values were not significantly different ($p > 0.3$). Consequently, no further analysis was performed on the values given in Table 2.

To determine a possible influence of MHQ on the hardness number, a comparison between the corresponding 25 pairs of values in Tables 1 and 2 was carried out. No clear-cut influence could be detected, but at CQ or DABA equal to 0.1% or 0.2%, the hardness numbers were higher in Table 1 than in Table 2 ($p < 0.01$). With the other numbers a trend in the opposite direction was present, although not statistically significant.

Discussion

The present results have shown significant influences of camphorquinone and amine on the hardness of light-curing polymers. The influence of camphorquinone and amine was particularly obvious at a low level of inhibitor, at which relatively large amounts of CQ and DABE were found to be beneficial with regard to hardness.

No studies on the level of inhibitor in restorative resins have apparently been published. The inhibitor level in light-curing materials may be assumed to be considerably lower than in chemically cured materials. In the latter type of materials, inhibitors are present to give working time (8) and to convey storage stability, especially of the benzoyl-peroxide-containing component (9). An inhibitor level of 0.025% is probably realistic for proprietary light-curing products. At this concentration of inhibitor, the influence of CQ and DABE was much less pronounced, giving a considerable freedom of choice in the formulation of the resins. Limits in the amount of amine may be set by the tendency to internal discoloration, which has been shown to increase with the concentration of amine (10). Limits in the amount of camphorquinone may be set by the yellowness of the cured material, which increases with the concentration of camphorquinone. Taking these factors into consideration, a concentration of CQ and DABE of 0.1–0.2% may yield optimal formulations. This level of CQ is in agreement with published values for camphorquinone in various composites (11).

A comparison between Table 1 and earlier data (2) shows that the hardness number obtained in the present study with CQ = amine = 0.5% is somewhat higher than earlier values obtained with a different amine. This may indicate that not only the quantity but also the type of amine is of importance for the mechanical properties of light-cured materials.

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