

Unpolymerized surface layers on sealants

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Oxygen inhibits radical polymerization, and for the present investigation, the thickness of the resulting unpolymerized surface layer on various proprietary dental polymers was measured by a microscopic technique. The inhibition depth of the polymerized resins varied from 7 to 84 μm . Resin systems with the tertiary aromatic amine 3,4-xylyldiethanolamine as the activator had a thinner unpolymerized layer than those with p-tolyldiethanolamine. Increased viscosity also resulted in reduced thickness of the unpolymerized films. UV-light cured resins had thinner inhibited layers than those of comparable viscosity with a peroxide-amine initiator system. However, the thinnest unpolymerized film was seen with a chemically activated resin system containing acetone.

This investigation has shown that the thickness of the unpolymerized film on cured dental resins is related to the composition and the initiating system.

Key-words: Dental polymers; oxygen inhibition; substituent constants; microscopy

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The inadequacy of some conventional dental sealants to polymerize in thin films on smooth tooth surfaces has been demonstrated previously (26). This inadequacy is mainly due to non-polymerization caused by oxygen inhibition of free-radical polymerization (6, 8, 21, 24, 25). It has been shown that the reactivity of oxygen to a growing radical is much higher than that of a monomer (24). Thus the polymerization reaction will start when the concentration of oxygen is strongly reduced. The presence of an uncured film on the surface of polymerized dental resins has been demonstrated (13, 20,

26). The purpose of the present investigation was to assess variations in the thickness of the uncured layer on eight polymerized proprietary resins, and to see whether this could be correlated with their composition (2–5, 22, 23).

MATERIALS AND METHODS

The proprietary resin materials listed in Table 1 were investigated. The materials with chemically induced polymerization were mixed according to the manufacturers' instructions. The mate-

Table 1. *Proprietary resins used in the investigation*

| Brand | Code | Batch no. | Manufacturer |
|------------------------------|------|-------------------------------|---------------------------------|
| Adaptic Bonding Agent | AB | 1204788K303 | Johnson & Johnson, NJ, USA |
| Adaptic Glaze | AG | 0206D145014 | Johnson & Johnson, NJ, USA |
| Delton Pit & Fissure Sealant | DS | 2147D4015003 | Johnson & Johnson, NJ, USA |
| Concise Enamel Bond | CE | base: 8131H1A cat: 8163H1B | 3 M Company, MN, USA |
| Concise White | CW | base: 71401 cat: 6233F1 | 3 M Company, MN, USA |
| Estilux Glaze | EG | 601229 | Kulzer & Co. GmbH, West Germany |
| Nuva Seal | NS | base: 74127 init: 74106 | L.D. Caulk Company, Canada |
| Saga Sealant | SS | Not indicated | Saga Orthodontics, Norway |

rials with ultraviolet (UV) light induced polymerization, NS and EG, were exposed to light from a UV-light source (Duralux UV-20A, Kulzer & Co. GmbH, W. Germany). The materials which were polymerized by chemical initiation were placed between a microscope slide and a cover slip after mixing. The UV-activated materials were also placed between a microscope slide and a cover slip, and were irradiated through the cover slip. The thickness of the cover slips were 1.50 ± 0.06 mm ($\bar{x} \pm S.D.$) and the transmittance was determined spectroscopically (DM 4 Double-beam spectrophotometer, Carl Zeiss, W. Germany) to be more than 90 per cent above 340 nm. During the inhibition period (24) and polymerization period the resin systems were exposed to air only at the resin boundary between the two glass plates (Fig. 1).

The method applied was a modified version of the microscopic technique presented by Finger and Jørgensen (13). It was essential that the microscope slide was in a horizontal position to avoid displacement of the layers during polymerization. Under these conditions the thickness of the polymerized films would range from 10 to 50 μm .

After polymerization the thickness of the unpolymerized film was measured in a transmission microscope (Orthoplan with Orthomat-W, Ernst Leitz

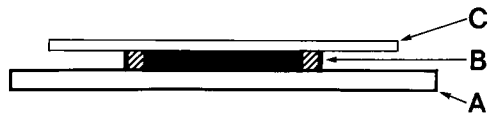


Fig. 1. Assembly for measuring inhibition zone. Microscope slide (A), resin with unpolymerized layer (B) and cover slip (C) on top.

GmbH, W. Germany) with a micrometer disc calibrated against a stage micrometer. The thickness of the unpolymerized film was recorded as the distance between the outer boundary and the interface between the polymerized and the unpolymerized resin.

The distinct line between polymerized and unpolymerized resin is caused by different refraction indices of the solid and the liquid material. The thickness of the unpolymerized film was measured at five different points on each specimen. Six specimens were made of each material.

RESULTS

A layer of unpolymerized material on polymerized dental resins was readily detected by transmission microscopy (Figs. 2-4). The unpolymerized film

Figs. 2-4. Micrographs of cured resins in contact with air (A), the inhibited layer (I) and polymerized material (S). The unfilled resins AB (Fig. 2), SS (Fig. 3) and the filled resin CW (Fig. 4) are represented.

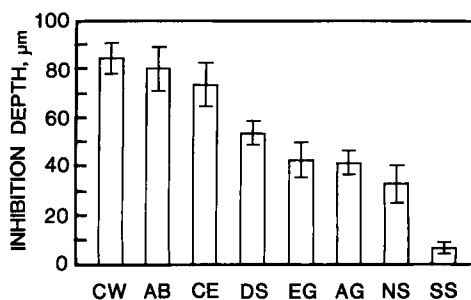
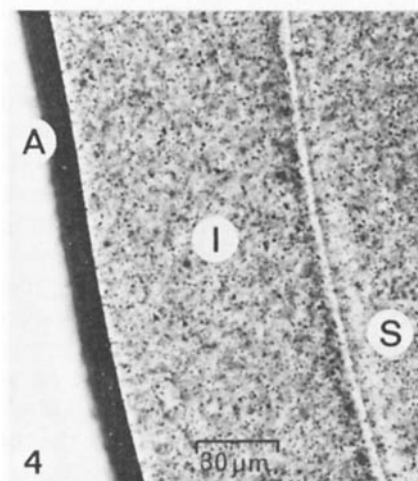
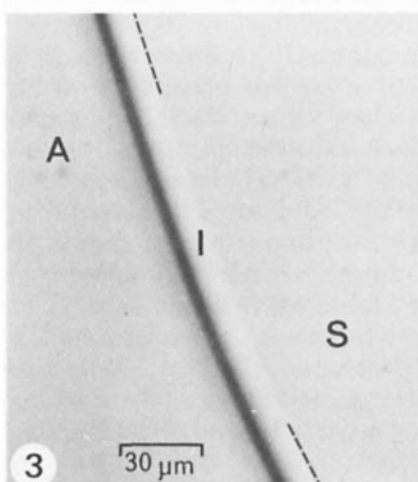
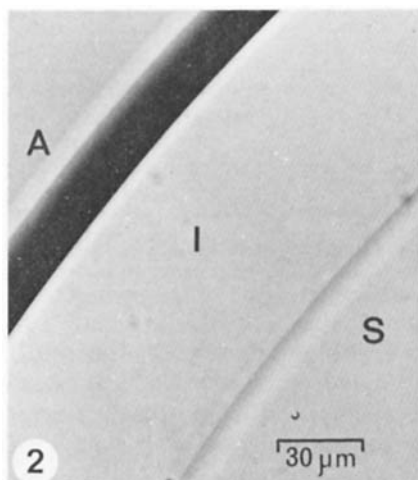


Fig. 5. The thickness of the unpolymerized layer on eight polymerized dental resin materials. Vertical lines on bars indicate standard deviations. Code, see Table 1.

thickness varied for the different resin materials as shown in Fig. 5. The thickness of the inhibition zone ranged from $7 \pm 2 \mu\text{m}$ ($\bar{x} \pm \text{S.D.}$) for the resin SS (Fig. 3) to $84 \pm 6 \mu\text{m}$ for the filled resin CW (Fig. 4).

Regarding the resins where the mean thickness of the inhibition layer was within the range of 33 to 53 μm (NS, AG, EG, DS) compared to the resins with an inhibition layer in the range of 73 to 84 μm (CE, AB, CW) the difference was statistically significant ($p < 0.001$, Student t-test). A statistically significant difference was also found between DS and AG ($p < 0.001$). SS had a significantly thinner inhibition layer than any of the other materials ($p < 0.001$).

DISCUSSION

The modified microscopic method (13) used in this investigation has been proposed (7) as a test method in a future standard for resin based pit and fissure sealants (International Organization for Standardization, Technical Committee 106, Working Group 1, Task Group 5). A relatively good correlation has been documented between the original microscopic method and a method based on the solubility of the unpolymerized part in ethanol (13).

The resulting thickness of the unpolymerized film of the various proprietary resin materials (Fig. 5) could be a result of differences in composition (2, 3, 22). The polymerization of the materials CW, AB and CE is chemically induced by means of benzoylperoxide and the tertiary aromatic amine p-tolyldiethanol amine (PTDEA) (4,23). The composition of the resin systems CE and CW are principally the same with respect to the organic part; the only difference being that CW contains 7.7 wt.-% inorganic fillers (22). The viscosity of CE and AB has been reported to be 0.28 and 0.20 Pa·s, respectively, at 23°C (3). Thus the viscosity of the liquid resins CW, AB and CE is of the same magnitude. According to the Stokes-Nernst-Einstein equation there is an inverse relationship between the diffusion coefficient and viscosity (16). Thus the rate of oxygen diffusion in a resin liquid decreases with increasing viscosity, and as the viscosity is of the same magnitude, the supply of oxygen to the reactive sites, i.e. the radicals, is of the same order of magnitude.

The resin DS has a monomer and peroxide composition similar to AB (3, 5, 22, 23), and a similar viscosity. One difference is that DS contains approximately 3 per cent of the tertiary aromatic amine 3,4-xylyldiethanol amine (XDEA), whereas AB has a similar amount of PTDEA (4, 23).

The actual type of free-radical polymerization is based on the reactivity of the tertiary aromatic amine in its reaction with benzoylperoxide which involves a one-electron transfer from amine to peroxide (10, 15). The initial step is probably the formation of a transfer complex between the aromatic amine and benzoylperoxide. The formation of charge-transfer complexes between aromatic amines and electron-accepting benzene derivatives varies with the nature of the substituents of

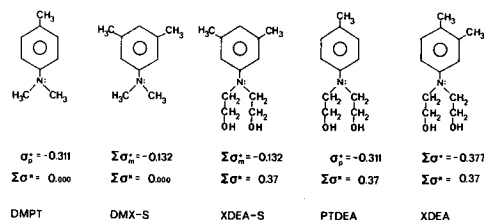


Fig. 6. Chemical formulas and substituent constants of the different tertiary aromatic amines. Code, see Table 2.

the electron-donating amine and the electronacceptor (1). Each substituent has a sigma (σ) value that reflects the electronic influence of the substituent to the reaction site (14, 17, 18). A maximum reactivity for amines with aryl substituents having a σ^+ value of approximately -0.20 or a Hammett σ value of -0.14 has been reported (9, 11, 12). These values refer to N,N-dimethyl substituted aromatic amines with the methyl groups having a σ^* value of 0.000 by definition. The $\Sigma\sigma^{*+}$ of the two 2-hydroxyethyl nitrogen substituents of the aromatic diethanolamines is calculated to be approximately 0.37, i.e. the $\Sigma\sigma^+$ value must be smaller than -0.20 to compensate for the electron-withdrawing influence of the 2-hydroxyethyl groups. The «hardening» times of composites based on dimethacrylate monomer formulations using different tertiary aromatic amines have demonstrated that DMX-S has a better activating ability than DMPT, Table 2 and Fig. 6 (9, 11, 12). XDEA-S leads to increased working time at 23°C compared to PTDEA (19). Accordingly XDEA, with $\Sigma\sigma^+ = -0.377$, has a better activating ability than PTDEA. Therefore the rate of radical formation must be increased with XDEA. The competitive reactions between free radicals with oxygen and monomers should be more favourable for an earlier start of polymerization with the material DS than with AB, which might explain the thinner inhibition zone seen with DS.

Table 2. *Tertiary aromatic amines*

| Amine | Code |
|---------------------------|--------|
| N,N-dimethyl-p-toluidine | DMPT |
| N,N-dimethyl-3,5-xylidine | DMX-S |
| p-tolyldiethanolamine | PTDEA |
| 3,5-xylyldiethanolamine | XDEA-S |
| 3,4-xylyldiethanolamine | XDEA |

Comparing the two materials AG and DS with respect to depth of oxygen inhibition, two effects should be considered, i.e. the effect of the initiator system and the viscosity. AG and DS have the same initiator system (4, 5, 23). However, the monomer liquids of AG contain less XDEA and benzoylperoxide than DS (4, 5, 23). The monomer composition, however, is not the same (3, 22). This difference in monomer composition results in a higher viscosity for AG than for DS. The viscosity of AG has been reported to be 1.67 Pa·s at 23°C (3), which is more than eight times greater than the viscosity of DS. Considering the inverse relationship between diffusion coefficient and viscosity (16) the result is that the inhibition layer on AG will be thinner than the layer on polymerized DS because of the reduced oxygen supply to the reactive sites.

According to monomer composition (22) EG should have a viscosity somewhat above 0.3 Pa·s, and NS has a viscosity of 0.45 Pa·s at 23°C (3). In spite of the relatively low viscosity the inhibited layer is not very thick. The polymerization of these two UV-light activated materials starts after only a few seconds, i.e. the rate of radical formation is much higher than in materials with chemically induced polymerization. In this way the dissolved oxygen is consumed fast and the rate of diffusion for exogeneous oxygen is low compared with the rate of radical formation.

The monomer containing component of SS has a composition similar

to NS (22). The other liquid component of SS is a solution of 5 wt.-% benzoylperoxide in acetone (23). When mixed in equal quantities a blanket of acetone vapor may form at the resin surface. This blanket of acetone vapor prevents direct access of air to the resin. In this way the supply of exogeneous oxygen is strongly reduced and the result is a very thin inhibition zone (Figs. 3 and 5). The resulting small inhibited layer for SS in the present investigation is in accordance with clinical results demonstrating that only the acetone-containing material could polymerize in thin films on tooth surfaces (26).

This investigation has shown that the applied microscopic technique is suitable as a routine test method for determining the unpolymerized layer on resin surfaces.

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