Factors Contributing to the Incompatibility Between Simplified-step Adhesives and Chemically-cured or Dual-cured Composites. Part III. Effect of Acidic Resin Monomers

Byoung I. Suha/Li Fengb/David H. Pashleyc/Franklin R. Tayd

**Purpose:** This study examined the polymerization kinetics of acid-contaminated light- and chemically-cured resins with the use of differential scanning calorimetry.

**Materials and Methods:** Light-cured and chemically-cured versions of an experimental bis-GMA/TEGDMA resin at the ratio (w:w) of 62:38 were prepared. Four acidic resin monomers with either carboxylic (DSDM and MAA) or phosphoric functional groups (MP and 2MP) were added at a 10 wt% concentration to these resins to simulate the intermixing of resin composites and unpolymerized acidic monomers along the adhesive-composite interface of simplified-step dentin adhesives. Different concentrations of the most acidic monomer 2MP (10 to 50 wt% for the light-cured resin, and 2 to 4 wt% for the chemically-cured resin) were also added to examine their contribution to reducing the extent and rate of polymerization of these resin mixtures. The effect of sodium benzene sulphinate on the polymerization of the chemically-cured resin that was contaminated with 10 wt% 2MP was also investigated.

**Results:** At 10 wt% concentration, all acidic monomers had a limited effect on the polymerization of the light-cured resin. The rate and extent of polymerization in the chemically-cured resin was substantially reduced by the carboxylic acid monomers DSDM and MAA, while polymerization was completely inhibited in the presence of the organophosphate monomers MP and 2MP. Substantial reductions in the rate and extent of polymerization of the light-cured resin occurred only in the presence of high concentrations (30 to 50 wt%) of 2MP. More acute polymerization inhibition was observed when the chemically-cured resin was contaminated with 2 to 3 wt% 2MP, with polymerization completely inhibited at 4 wt%. Addition of sodium benzene sulphinate to 2MP-contaminated chemically-cured resin revived the previously uncured resins, but their rate and extent of polymerization were still inferior to that of uncontaminated chemically-cured resin.

**Conclusion:** When the influence of adhesive permeability was excluded with the use of neat, water-free resins, deactivation of the tertiary amine utilized in the chemically-cured resin by even very low concentrations of acidic resin monomers accounts for the reported incompatibility between simplified-step dentin adhesives and chemically-cured composites. The polymerization of light-cured resin is only affected by much higher concentrations of acidic resin monomers.

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Contemporary dentin adhesives all contain hydrophilic resin monomers to improve their affinity for hydrophilic substrates such as dentin. There are two types of hydrophilic monomers: neutral and acidic (ionic). 2-Hydroxyethyl methacrylate (HEMA) is an example of a water-soluble, neutral hydrophilic monomer with a hydroxyl (-OH) functional group. Acidic monomers used in dental adhesives may be further divided into three categories: those with carboxylic (-COOH) functional groups (e.g., 4-methacryloxyethyl trimellitic acid anhydride [4-META]), those with phosphoric (-O-P-(OH)(OR)) functional groups (e.g., dipentaerythritol-pentaacrylate phosphate ester [PENTA]), and those with sulfonic (-SO3H) functional groups (e.g., 2-acrylamido-2-methylpropane sulfonic acid [AMPS]). For totally-cured composites, and/or create a hypermeasurable adhesive layer. Depending on the bondability of the former phenomenon is independent of the type of bonding substrate, water blistering that represents the consequence of the latter phenomenon is only observed along the adhesive/composite interface when bonding is performed on hydrated dentin. Adverse acid-base reaction may be circumvented with the use of ternary catalysts, such as the sodium salts of aryl sulphonic acids. This remedial strategy is being adopted in most 2-step total-etch adhesives by the inclusion of separate bottles of activator solution containing a ternary catalyst, and in some 1-step self-etch adhesives by the incorporation of different types of ternary catalysts as integral adhesive components. Nevertheless, when these activated adhesives are employed for bonding to hydrated dentin, increased adhesive permeability still accounts for the decrease in bond strengths of both chemical/dual-cured and light-cured composites that are in prolonged contact with the cured activated adhesives prior to polymerization.

We have shown in Part I and II of this series that the consequences of both adverse acid-base reaction and adhesive permeability were more acute in a 1-step self-etch adhesive than in a 2-step total-etch adhesive, by virtue of the higher concentration or the more acidic nature of the ionic resin monomers that are present in the former. As both phenomena were involved in bonding to hydrated dentin, it was difficult to examine each phenomenon in isolation without the influence from the other. We envisage that a better understanding of the role played by adverse acid-base reaction may be obtained through the use of neat, water-free, un-bonded resin blends that are contaminated by acidic resin monomers to simulate a scenario that is likely to occur along the adhesive/composite interface.

Thus, the objectives of this study were to analytically examine the inhibitory effect of acidic monomers on the polymerization of light-cured and chemically-cured resin systems, and the enhancing effect of a ternary catalyst, sodium benzene sulfinate (SBS), on the polymerization of the acidic monomer-contaminated chemically-cured resin. This is accomplished with the use of differential scanning calorimetry (DSC), which measures the heat generated during resin polymerization. The null hypothesis tested was that the polymerization kinetics of light-cured and chemically-cured resin blends are not affected by the contamination of different types or concentrations of acidic resin monomers.
MATERIALS AND METHODS

Experimental Resin Systems

To ensure that the results of the light-cured and chemically-cured experiments were mutually comparable, light-cured and chemically-cured versions of an experimental bis-GMA/TEG-DMA (bisphenol diglycidyl ether dimethacrylate/triethylene glycol dimethacrylate) resin system were first fabricated. The exact compositions of these uncontaminated resin systems are shown in Table 1.

Four acidic resin monomers were added to the control resin blends in different weight percentages. They served as contaminants to simulate the scenario of contamination of light- and chemically-cured resin composites by uncured acidic adhesive resin monomers along the intermixed zone of the adhesive/composite interface. They consisted of two resin monomers with mono- and di-carboxylic acid functional groups that are less acidic (MAA and DSDM), and two organophosphate monomers (MP and 2MP) that are considerably more acidic (Table 2). The acidities of these water-free, nonionized acidic resin monomers were measured by dissolving them with a solvent that consisted of 70% absolute ethanol and 30% distilled water. Each acidic monomer was combined with the solvent in a 40:60 ratio (ie, 2 g of material and 3 g of solvent). The solution was thoroughly mixed for 5 min using a magnetic stirrer, and measured at ambient temperature with a pH meter (Model 7132BN, Thermo Orion, Beverly, MA, USA) that was calibrated with the appropriate buffer solutions.

As the incorporation of high concentrations of these acidic monomers resulted in a dilution of the photoinitiator system in the experimental light-cured resin, a photoinitiator-free resin blend consisting of pure bis-GMA/TEG-DMA (62:38) was additionally produced as a control diluent. It was added to the original light-cured resin blend in a separate experiment to investigate the effect of dilution of the photoinitiator system on resin polymerization. As only very low concentrations of acidic monomers were added to the chemically-cured resin, this procedure was not adopted.

Table 1 Composition of the light-cured and chemically-cured resin systems examined in this study

<table>
<thead>
<tr>
<th>Components</th>
<th>Light-cured resin</th>
<th>Chemically-cured resin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Part A: Catalyst component</td>
<td>Part B: Base component</td>
</tr>
<tr>
<td>Resin monomers</td>
<td>bis-GMA (61.2%)*</td>
<td>bis-GMA (60.6%)</td>
</tr>
<tr>
<td></td>
<td>TEG-DMA (37.5%)</td>
<td>bis-GMA (61.0%)</td>
</tr>
<tr>
<td>Catalysts</td>
<td>CQ (0.3%)</td>
<td>BPO (2.2%)</td>
</tr>
<tr>
<td></td>
<td>EDMAB (1.0%)</td>
<td>–</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>MEHQ (200 ppm)</td>
<td>BHT (1500 ppm)</td>
</tr>
</tbody>
</table>

* Values are expressed as weight percentages

1 Esschem, Linwood, PA, USA
2 Hampford Research, Stratford, CT, USA
3 ATOPNA Chemical, Philadelphia, PA USA
4 Lancaster Synthesis, Windham, NH, USA
5 TCI America, Portland, OR, USA
6 Aldrich Chemical, Milwaukee, WI, USA

Abbreviations: bis-GMA: bisphenol A diglycidyl ether dimethacrylate; BHT: butylated hydroxytoluene; BPO: benzoyl peroxide; CQ: camphorquinone (photosensitizer); EDMAB: ethyl dimethyl aminobenzoate (tertiary amine photoaccelerator); MEHQ: monomethyl ether hydroquinone; p-TID: para-tolyl imino diethanol (tertiary amine co-initiator for chemical-cured resin); TEG-DMA: triethylene glycol dimethacrylate
Experimental Setup for Examining the Polymerization of Light-cured Resins

A differential scanning calorimeter (Shimadzu DSC-50, Kyoto, Japan) was used to measure the heat of polymerization as a function of the extent of polymerization of the different resin blends. For the light-cured resins, the setup was modified to overcome the difficulty experienced in differentiating the heating effect of the light source from the heat generated by resin polymerization. As photopolymerization was performed at about ambient temperature and no thermal shielding was necessary, the DSC unit was modified by replacing the cell cover and the furnace lid with a 50 x 50 x 6 mm glass plate (Fig 1).

A halogen light-curing unit (Variable Intensity Polymerizer, Bisco, Schaumburg, IL, USA) was positioned with the curing tip located at 25 mm above the detector plate of the DSC unit. This generated an output intensity of 60 mW/cm² over the uncured resin specimens when the light output was set at

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**Table 2** Acidic resin monomers that were used as contaminants of the light-cured and chemically-cured resins

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Acidic resin monomers</th>
<th>Structural formulae</th>
<th>pH values</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSDM</td>
<td>Dicarboxy dimethacryloyloxy ethyl diphenyl sulfone&lt;sup&gt;a&lt;/sup&gt;</td>
<td><img src="image" alt="Structural formula" /></td>
<td>3.35</td>
</tr>
<tr>
<td>MAA</td>
<td>2-Methacrylic acid&lt;sup&gt;b&lt;/sup&gt;</td>
<td><img src="image" alt="Structural formula" /></td>
<td>2.40</td>
</tr>
<tr>
<td>MP</td>
<td>Ethylene glycol methacrylate dihydrogen phosphate&lt;sup&gt;b&lt;/sup&gt;</td>
<td><img src="image" alt="Structural formula" /></td>
<td>0.86</td>
</tr>
<tr>
<td>2MP</td>
<td>Bis[2-(methacryloyloxy)ethyl] phosphate&lt;sup&gt;b&lt;/sup&gt;</td>
<td><img src="image" alt="Structural formula" /></td>
<td>0.79</td>
</tr>
</tbody>
</table>

<sup>a</sup> Synthesized by Bisco Inc (Schaumburg, IL, USA).

<sup>b</sup> Purchased from Aldrich Chemical Co (Milwaukee, WI, USA) and used without further purification.

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Fig 1  Modification of the differential scanning calorimeter to examine heat generation during the polymerization of light-cured resins.
400 mW/cm\(^2\). To ensure that both the reference
and detector plates received exactly the same
amount of light energy, the position of the light-curing
unit was carefully adjusted so that the heat flow re-
corded by the DSC unit was within 0.00 ± 0.05 mW
when two empty aluminum lids of the sample cruci-
bles were placed over the detector plates (ie, in the
absence of the reference and sample specimens).
After calibration, neutral density filters were used to
further reduce the intensity from 60 mW/cm\(^2\) to
15 mW/cm\(^2\). The use of a lower output intensity fur-
ther increased the level of confidence of our mea-
surements to within 0.00 ± 0.03 mW.
A small amount (4 to 8 mg) of the unpolymerized
sample resin specimen was placed on an alumi-
um lid. A well-polymerized resin of a similar mass
was placed on an identical aluminum lid and used
as the reference specimen. This was based on our
previous observations that high reproducibility of
the thermograms was achieved when an additional
reference specimen was used instead of the empty
aluminum lid.
Prior to recording the heat flow, the furnace and
the glass plate were initially covered with a piece of
aluminum foil to block the ambient light. Nitrogen
was then introduced at a flow rate of 20 ml/min to
prevent the effect of oxygen inhibition on free rad-
cal-initiated polymerization. Purging was performed
for at least 6 min during the period of temperature
rise from ambient temperature to the isothermal
temperature of the DSC unit that was set at 25ºC.
The aluminum foil was removed as the isothermal
temperature was reached. Each light-cured resin
specimen was irradiated for 100 s at 15 mW/cm\(^2\),
yielding a total radiant energy of 1.5 J. The reduced
power output to the unfilled resin was thus compen-
sated by a prolonged exposure time\(^{11}\) to provide a
dose of radiant energy that was roughly equivalent
to that received by a filled resin composite at 1 to
2 mm beneath the irradiated surfaces.\(^{15,28}\)

**Experiments Performed with Light-cured Resins**

Three experiments were performed using the exper-
imental light-cured system.

1. **Effect of the acidity of contaminated resin
monomers on polymerization**

This series of experiments was performed using
the four different acidic monomers (DSDM, MAA,
MP and 2MP) with increasing acidity. 10 wt% of
each acidic monomer was added to the control
light-cured resin, producing four contaminated resin
blends. They were compared with the undiluted,
uncontaminated control light-cured resin. Five runs
were performed for each resin blend, with the tem-
perature and heat flow recorded up to a period of
20 min after the commencement of photopolymer-
ization.

2. **Effect of the acidic resin monomer concen-
tration on polymerization**

This series of experiments was performed using
different concentrations of the most acidic resin
monomer 2MP (10 wt%, 20 wt%, 30 wt%, and 50
wt%). The four contaminated resin blends were
compared with the undiluted, uncontaminated con-
trol light-cured resin in the manner previously de-
scribed.

3. **Effect of dilution of photoinitiator system**

This series of experiments was performed to en-
sure that reduction in the rate and extent of poly-
merization in the acidic monomer-contaminated res-
in blends were not caused by a dilution of the pho-
toinitiator system of the original light-cured resin.
Different concentrations of the photoinitiator-free
bis-GMA/TEG-DMA diluent (33 wt%, 50 wt%, and 67
wt%) were added to the control light-cured resin, pro-
ducing three diluted resin blends. They were com-
pared with the original undiluted light-cured resin in
the manner previously described.

**Experimental Setup for Examining the Polymer-
ization of Chemically-cured Resins**

For chemically-cured resins, the instrument was
used without modification. Unlike a light-activated
system in which the initiation of polymerization oc-
curs on demand, there was a problem in attempting
to match the induction period of the chemically-
cured period with the period of thermal equilibra-
tion of the DSC unit. The induction period is repre-
sented by the working time of a chemically-cured
resin, during which the generated free radicals are
consumed by the inhibitors until the latter are de-
pleted before polymerization occurs. To minimize
the time for equilibrating the specimen tempera-
ture, a pre-polymerized dummy specimen was first
placed inside the DSC chamber, after which the
chamber was allowed to attain operating tempera-
ture (25ºC). Equal portions of the base and catalyst
components of the chemically-cured resins were
 briskly mixed for 10 s and placed immediately into
the DSC chamber to replace the dummy specimen.
The mass of the polymerized specimen was weighed after the end of measurement.

Despite the high concentration of inhibitors (Table 1) and short period of mixing, polymerization of the uncontaminated chemically-cured resin mixture sometimes occurred before optimal thermal equilibrium of the DSC chamber could be achieved, making the determination of the baseline of chemical polymerization difficult.

For this reason, baseline was arbitrarily designated as that of the dummy specimen (Appendix I). This reduced the accuracy in using DSC measurements for quantifying the degree of conversion of the chemically-cured resins. Nevertheless, the thermograms generated were reproducible and allowed meaningful comparisons to be made with the acidic monomer-contaminated chemically-cured resins.

Experiments Performed with Chemically-cured Resins

Three experiments were performed using the experimental chemically-cured system.

4. Effect of the acidity of contaminated resin monomers on polymerization

This series of experiments was performed using the four different acidic monomers (DSDM, MAA, MP, and 2MP) with increasing acidity. 10 wt% of each acidic monomer was mixed with the catalytic component (Part A) of the chemically-cured resin and stored in dark for 5 min prior to mixing with the base component (Part B). The four contaminated resin blends were compared with the undiluted, uncontaminated chemically-cured resin (control). The induction periods, which represent the working times of the chemically-cured resins, were recorded during the course of heat flow measurements (Appendix I) but were not included in the presentation of the polymerization exotherms.

5. Effect of the acidic resin monomer concentration on polymerization

This series of experiments was performed using different concentrations of the most acidic resin monomer 2MP (2 wt%, 3 wt%, and 4 wt%). The three contaminated resin blends were compared with the control (undiluted, uncontaminated chemically-cured resin) in the manner previously described.

To further substantiate that the acidity of the resin monomer is the sole contributing factor to polymerization inhibition, a chemically-cured resin blend contaminated with 5 wt% 2MP (FW = 322) was prepared. A basic tertiary amine DBAE (2-(dibutylamino) ethanol; FW = 173, purity 99%, Aldrich Chemical, Milwaukee, WI, USA) was added to the contaminated resin blend in different concentrations (1.2% and 2.5%) in order to neutralize the effect of the acidic resin monomer 2MP. Based on their formula weights, 1 g of DBAE can neutralize about 2 g of 2MP. Thus, the contaminated resin with 2.5% DBAE theoretically should have very little free 2MP where- as the one with 1.2% DBAE should have about 2.5% non-neutralized 2MP.

6. Effect of the addition of SBS on the polymerization of an acidic monomer-contaminated chemically-cured resin

This series of experiments was performed by mixing different concentrations of SBS (0.2 wt%, 0.6 wt%, and 2 wt%) with a chemically-cured resin that was contaminated with 10 wt% 2MP. Sodium benzene sulphinate (C₆H₅NaO₂S) (ICN Pharmaceuticals, Costa Mesa, CA, USA) was used without further purification. As the 2MP was already incorporated in the catalytic component (Part A), the SBS was dissolved in acetone/water and added to the base component (Part B) of the chemically-cured resin. The solvent was allowed to evaporate, leaving behind a white precipitate within the base resin. The
three SBS-containing, acid-contaminated chemically-cured resins were compared with the undiluted, uncontaminated chemically-cured control in the manner previously described.

**Data Conversion from Heat Flow to Exotherm**

The DSC thermogram recorded the heat flow (mW or mJ/s) as a function of time. For easier interpretation of the kinetics of resin polymerization, the heat flow data was converted to the enthalpy of polymerization (exotherm) and expressed in J/g (Appendix II).

**Statistical Analyses**

For each experiment, the extent of polymerization, represented by the maximum exotherm for each polymerized resin, and the normalized rate of polymerization, represented by the maximum heat flow per unit mass from the original thermogram, were computed. Where appropriate, linear or logarithmic regression analyses were performed to correlate the pH values of the acidic monomers or the concentration of the most acidic monomer 2MP with the extent and rate of resin polymerization, with statistical significances set at $\alpha = 0.05$.

**RESULTS**

The pH values of the four acidic resin monomers are shown in Table 2. Representative polymerization exotherms of light-cured resins that were contaminated with 10 wt% of different types of acidic monomers (experiment 1) are shown in Fig 2. At this concentration, the addition of DSDM, MAA, MP and 2MP had limited effects on the polymerization of light-cured resins.

![Fig 2](image-url)
The effect of dilution of the light-cured catalyst with high concentrations of photoinitiator-free resin of the same resin blend (experiment 3). Although a significant linear correlation ($p < 0.05$) between the extent (Fig 4b) and rate of polymerization (Fig 4c) and the concentration of the diluent could be observed, the inhibition effects of resin dilution were mild when compared to those that were caused by acid-contamination of the light-cured resins. There were also highly significant correlations ($p < 0.01$) between the concentrations of the acidic monomer contaminant and the maximum exotherm (Fig 4b) and the maximum heat flow (Fig 4c) produced during the polymerization of the contaminated light-cured resins.
Unlike the light-cured version, polymerization of the chemically-cured version of the experimental resin system was affected to different extents by the inclusion of 10 wt% of different acidic resin monomers (experiment 4). Whereas polymerization was only slightly inhibited by the less acidic mono- and dicarboxylic acid monomers MAA and DSDM, the more acidic organophosphates MP and 2MP completely destroyed the curability of the chemically-cured resin. Logarithmic regression analysis revealed a highly significant correlation between the maximum exotherm achieved after polymerization of the contaminated chemically-cured resin and the pH values of these acidic monomers (Fig 5b).

Although the chemically-cured resin did not polymerize when contaminated with 10 wt% 2MP polymerization did occur but was severely compromised with the addition of 2 to 3 wt% 2MP (experiment 5). Polymerization was completely inhibited with the inclusion of 4 wt% 2MP (Fig 6a). A substantial increase in the induction times of the chemically-cured resins was also observed with the inclusion of increasing concentrations of 2MP (Fig 6a). Linear regression analyses also revealed significant correlations (p < 0.05) between the concentrations of the 2MP contaminant, and the extent (Fig 6b) and the rate of polymerization (Fig 6c) of the chemically-cured resin. The difference in the rates of polymerization of the control and acid-contaminated light- and chemically-cured resin versions could be readily seen when their corresponding regression lines were compared in Fig 6d. A comparison of the regression lines exhibited by the contaminated light-cured and chemically-cured resin versions revealed that they exhibited the same slope (ie, the same rate of decline of the polymerization rate) but different intercepts.

The effect of neutralizing the effect of 2MP with DBAE is illustrated in Fig 7. Consistent with the previous observation, addition of 5% 2MP completely eradicated the curability of the acid-contaminated resin blend. The addition of 1.2% DBAE to the contaminated resin resulted in partial recovery of the polymerization of the resin blend. After 2MP was neutralized completely with 2.5% DBAE, both the rate and extent of polymerization of the resin blend was completely recovered.

The effect of different concentrations of SBS on the polymerization of the uncurable 10% 2MP-contaminated chemically-cured resin (experiment 6) is depicted in Fig 8. The inclusion of SBS of increas-
ing concentrations effectively revived and improved the polymerization of the previously uncurable, acid-contaminated resin. The induction time that preceded effective polymerization was also substantially shortened with increasing concentrations of SBS. Even with the addition of 2 wt% SBS, the extent and the rate (as exhibited by the slopes of the ascending part of the traces) of polymerization did not reach the same levels that were exhibited by the contaminated chemically-cured resin.

**DISCUSSION**

We used DSC to examine the polymerization kinetics of acid-contaminated resins. This technique has similarly been employed in other recent studies of methacrylate-based resins.\(^{10,17,23}\) The DSC technique avoids potential interference from the filler components when polymerization of resin composites is examined with Fourier transform infrared spectroscopy (FTIR),\(^{2,5,13}\) although the unfilled res-
ins employed in this study were unaffected. The DSC technique also provides a simple means of determining the degree of conversion in dental restorative resins that lack functional groups that can act as internal standards for FTIR assessment.\textsuperscript{27} The rationale of the DSC technique is based on the fact that the exothermic heat of reaction (enthalpy) arising from the free-radical addition polymerization of methacrylate monomers is proportional to the number of vinyl groups involved, thus allowing the degree of conversion in these resins to be determined. As the resin sample in the present study was polymerized in a flat-bottomed aluminum lid, this allowed us to evaluate the degree of conversion using FTIR by placing the flat polymerized surface directly over the attenuated total reflection (ATR) window of the spectrophotometer. To ensure that there was optimal polymerization of the uncontaminated light-cured resin when it was irradiated with 15 mW/cm\textsuperscript{2} for 100 s, for example, we also compared the degree of conversion derived from the DSC measurement (ie, the ratio of the maximum exotherm and the theoretical value for maximum conversion of the double bonds) with that determined by FTIR. A $68.0 \pm 1.3\%$ conversion was obtained by DSC, versus a $63.9 \pm 0.9\%$ conversion as measured by FTIR. As both values were within the typical range (55\% to 75\%) of double bond conversions for multifunctional dental restorative monomers,\textsuperscript{1} we confirmed that the light-cured version of the experimental resin was adequately polymerized upon prolonged irradiation with a low power output in an inert nitrogen atmosphere. The higher degree of conversion obtained by DSC compared with FTIR was similar to that reported (5\% to 7\%) by Imazato et al.,\textsuperscript{13} and is probably caused by the enthalpy contribution from low molecular-weight, unsaturated impurities that are present in the bis-GMA/TEG-DMA resin mixtures.

Polymerization kinetics is expressed as both the rate and extent of polymerization, as these parameters may not proceed at the same pace in vinyl free-radical addition polymerization.\textsuperscript{4} The rate of polymerization is the speed of the reaction and the extent of polymerization represents how thorough the reaction process is. In the original thermograms (Appendix II), the peak height of heat flow normalized by sample mass represents the maximum rate of polymerization. While this value was employed in the regression analyses, similar results may also

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**Fig 7** Effect of neutralization of the acidic monomer 2MP with a basic tertiary amine, DBAE (2-(dibutylamino) ethanol), on the polymerization of the chemically-cured resin (experiment 5). The addition of 2.5\% DBAE to the resin contaminated with 5\% 2MP completely prevented the polymerization inhibition exhibited by the acidic resin monomer.

**Fig 8** Representative polymerization exotherms of 10 wt\% 2MP-contaminated chemically-cured resins that were polymerized in the presence of different concentrations of sodium benzene sulphinate (SBS) (experiment 6). The uncontaminated chemically-cured resin was used as the control with the further addition of SBS. The values in parentheses are the estimated induction times. SBS effectively enhanced the curability of the contaminated chemically-cured resin that did not polymerize in the absence of SBS (Fig 5a).
be derived from the exotherms by comparing the rates (heat flow/mass) at any specific time during the rapid curing period, which is roughly the first 1 min for the light-cured and the first 5 to 10 min for the chemically-cured resins. The maximum exotherm in our study only represents the extent of polymerization that was achieved immediately after curing. Depending on the concentration of TEG-DMA in the bis-GMA/TEG-DMA resin mixture, the extent of polymerization may further improve upon storage for up to 24 h. As substantial differences in the maximum exotherms were observed among the control and the acid-contaminated resins (Figs 3, 5, and 6), we do not anticipate any deviation from our interpretation of the results after postcuring maturation of the specimens.

As the polymerization kinetics of both the light-cured and the chemically-cured versions of the experimental resin system were affected by acid contamination, we have to reject the null hypothesis. However, it is also apparent from the DSC results that polymerization of the acid-contaminated light-cured resin was inhibited to a much lower extent than the corresponding acid-contaminated chemically-cured resin. This provides the raison d’être for the reported incompatibility between simplified-step adhesives and chemically-cured composites when they are bonded to dehydrated dentin or processed composites (i.e., without the complementary influence from adhesive permeability). Acidic resin monomers with carboxylic or phosphoric acid functional groups are frequently utilized as primer components in total-etch adhesives. The aggressiveness of contemporary self-etch adhesives is influenced by the acid dissociation constants (pKa) of the acidic resin monomers, as well as the increased concentrations of these acidic resin monomers. The effect of the former was investigated in experiments 1 and 4 (above) in which all the acidic monomers were used at the same concentration. Although they had a negligible detrimental effect on the rate and extent of polymerization of the light-cured resin, the organophosphates were much more aggressive than the carboxylated methacrylate monomers in inhibiting the polymerization of the chemically-cured resin. This is a reasonable expectation as the first pKa of unsubstituted carboxylic acid monomers are usually in the order of 10\(^{-5}\), while those of the organophosphates are in the order of 10\(^{-3}\).

We also tested the thermal curability of the unpolymerized chemically-cured resin that was contaminated with 10 wt% 2MP (Appendix III). As the acid-contaminated resin mixture could be polymerized by raising the DSC temperature to above 80°C, it was the tertiary amine p-TID, and not the benzoyl peroxide that was completely deactivated by 2MP. The results of experiments 1 and 4 also confirmed that light-cured composites are not affected by the concentration of acidic resin monomers that are usually present in 2-step total-etch adhesives, and that adverse acid-base reaction is not the reason for the exponential drop in bond strengths observed when a light-cured composite is left for an increasingly long period of time on the surface of hydrated dentin bonded with 1-step self-etch adhesives before it is polymerized.

The results of the present study further demonstrated that light-cured resins are not totally immune to adverse acid-base reaction when a tertiary amine is utilized as an accelerator for the camphorquinone photosensitizer. This can be seen from the results of experiments 2 and 5, when both the light- and chemically-cured resin mixtures were examined after contamination with increasing concentrations of the same acidic monomer. Although
the polymerization of both resin versions were inhibited by 2MP; a much higher concentration of 2MP (30 to 50 wt%) was required to substantially inhibit the polymerization of the light-cured resin (Fig 3). On the contrary, the inclusion of as little as 4 wt% 2MP resulted in complete deactivation of the tertiary amine p-TID in the chemically-cured resin (Fig 6a). The tertiary amine EDMAB in the light-cured resin is a weaker Lewis base compared with the p-TID in the chemically-cured resin, due to the presence of a more electronegative (electron-withdrawing) functional group at the para position (i.e., \(-\text{C(O)}\ CH_2\text{CH}_3\) for EDMAB vs \(-\text{CH}_3\) for p-TID). Thus, it is logical to assume that the acid-contaminated light-cured resins were better polymerized due to the use of an amine that is less reactive with acids.

However, a closer examination of the rate of polymerization of the two acid-contaminated resin versions revealed that the two regression lines exhibited the same slope but different intercepts (Fig 6d). The slopes of these regression lines represent the extent to which the rate of polymerization is affected by the deactivation of the tertiary amines. Therefore, if one were to add 2% to 4% of 2MP to both the light-cured and chemically-cured resins, the EDMAB would have been deactivated to the same extent as the p-TID. This raises the question why the light-cured resin still retained limited curability upon the addition of 50 wt% of a moderately acidic monomer such as 2MP. As the lone pair of electrons in a tertiary amine is responsible for both charge transfer during photoinitiation\(^6,22\) and redox reaction during chemical initiation,\(^20\) it should not be available for either process after being consumed in an acid-base reaction. A comparison of the intercepts of the regression lines, on the other hand, revealed that the actual rate of polymerization of the light-cured resin was approximately 10 times that of the chemically-cured resin. The difference between the rate of polymerization of the light- and chemical-resins remained the same up to the point when the chemically-cured resin was totally inhibited by 4 wt% of 2MP (Fig 6d). The concentration of photoinitiators used in the present study (camphorquinone 0.3 wt% and EDMAB 1.0 wt%) is considered to be an optimized concentration that is normally employed for the polymerization of light-cured resins.\(^28\) One possible explanation is that unlike a chemical initiator system in which the BPO-tertiary amine is consumed in more or less the same molar ratio in a redox reaction, less tertiary amine may be required for charge transfer to generate enough free radicals for the initiation of photopolymerization. The amount of non-neutralized EDMAB that remains in the light-cured resin may be sufficient to participate in charge transfer with the excited camphorquinone, resulting in a reduced but reasonable rate of polymerization upon contamination by acidic monomers. This hypothesis merits further testing and may be accomplished in future studies by monitoring the rates of polymerization of acid-contaminated light-cured resins that are formulated with decreasing concentrations of tertiary amines.

Irrespective of the cause of retained curability in the acid-contaminated light-cured resins, it is pertinent to point out that both the extent (Fig 4b) and rate of polymerization (Fig 4c) were compromised with increasing concentrations of a moderately acidic organophosphate diester such as 2MP. Moreover, the rate of polymerization of the light-cured resin was more acutely affected by acid contamination than the extent of polymerization. Throughout this study, we have concentrated on the use of our acid-contaminated resin model to simulate what may occur along the adhesive-composite interface in simplified-step dentin adhesives. However, it is rational to project our findings to represent what may also occur during the polymerization of contemporary light-cured self-etch adhesives. Higher concentrations of more acidic monomers are often utilized to render these adhesives aggressive enough to etch through thick smear layers\(^16\) and unground enamel.\(^14\) Although these monomers are originally diluted by adhesive solvents, one needs to consider that for a hypothetical light-curable 1-step self-etch adhesive that contains 20 wt% of 2MP dissolved in 60 wt% solvent, there will be up to 50 wt% of 2MP in the adhesive resin mixture after solvent evaporation, although some of these acidic components may be buffered by calcium ions when the adhesives are applied to tooth structures.

Based on the results of this study, two potential clinical consequences may arise if a tertiary amine is solely employed as the photoaccelerator in these highly acidic adhesives. The first is that these adhesives may exhibit longer postirradiation maturation times due to the acute reduction in their initial rates of polymerization. This may also undermine the ability of these hypothetical adhesives to resist polymerization shrinkage stresses during the critical stages of early composite coupling.\(^6\) The second is that these acidic adhesives will be less optimally polymerized compared with acid-free resin...
mixtures such as the bonding resin layers that are used in conventional-step adhesives. The lower degree of conversion and the increase in mobility of the polymer chains in these less optimally polymerized adhesive layers may increase their affinity for retention of water via hydrogen bonding. This may account for the two modes of nanoleakage identified within the adhesive layers of some 1-step self-etch adhesives that are morphological manifestations of the increased permeability in these adhesive systems. A less optimally polymerized adhesive may also increase its susceptibility to water sorption and resin and/or photoinitiator elution that in return hasten the hydrolytic degradation of resin-dentin bonds.

The use of sulphinic acids as ambient-temperature polymerization initiators for vinyl monomers such as methyl methacrylate and styrene dates back to the work of Hagger. He also patented a cavity-sealing solution containing glycerophosphoric acid dimethacrylate and methacrylic acid that was polymerized with a sulfinic acid initiator. This cavity-sealing solution was subsequently investigated by McLean and Kramer. Most of the 2-step total-etch adhesives are now supplemented with an additional bottle of activator solution containing the sodium salt of aryl sulphinic acid to enable them to bond to chemically-cured or dual-cured composites. As a co-initiator or ternary catalyst, the sodium salt of aryl sulphinic acid can react with acidic resin monomers to produce either phenyl or benzene sulphonyl free radicals that initiate the polymerization of chemically-cured composites.

In the present study, the effectiveness of SBS could be seen by its ability to revive unpolymerized chemically-cured resins that were contaminated with 10 wt% 2MP (Fig 8). A significant contribution of SBS is that it considerably shortened the induction time that occurred prior to the commencement of polymerization of the chemically-cured resins. Although both the rate and extent of polymerization of the acid-contaminated resin continued to improve up to 2 wt% of SBS, polymerization of these resins was still suboptimal when compared with the uncontaminated chemically-cured resin (control). As SBS is often used to render simplified-step dentin adhesives dual-curable for bonding to light-inaccessible areas such as root canals, the clinical consequence of a potentially weaker bond should be borne in mind.

In conclusion, we have demonstrated in this study that amine co-initiated light- and chemically-cured resin systems polymerize differently in the presence of acidic resin monomers. As the resin mixtures examined in the present study are essentially water-free systems, it is interesting to observe that neutralization of the tertiary amines by acidic resin monomers can still occur. As there are no "free" ions in the absence of water or a high dielectric medium, these interactions probably occur via ion-pair formation, as an ionic group is always associated with another of the opposite charge.

Whereas deactivation of the tertiary amines is responsible for the incompatibility between simplified-step adhesives and chemically-cured composites, the same phenomenon cannot account for the water blistering that occurs along the adhesive-composite interface when light-cured composites are applied to hydrated dentin bonded with these adhesives in a delayed light-activation mode to simulate the slower rate of polymerization of chemically-cured resin composites. The oxygen inhibition layer in simplified-step adhesives thus acts both as a source of acidic resin monomers that is responsible for deactivation of the tertiary amines, and as a hypertonic medium that triggers osmotic fluid transport through the permeable adhesive layer. It would be of clinical significance to examine whether the phenomena of acid-base incompatibility and water blistering can be eliminated in adhesive-bonded dentin that is devoid of an oxygen inhibition layer. This may be achieved by either removing the oxygen inhibition layer from the polymerized adhesive, or polymerizing the adhesive in an inert nitrogen atmosphere. While the former procedure is only feasible clinically, we favor the latter technique for in vitro investigations, due to the uncertainty in assuring the presence of an adequate layer of polymerized adhesive beneath the uncured oxygen inhibition layer in some adhesive systems. This may complicate our investigation by creating direct contact of the resin composites with the hybridized dentin.

Our preliminary study shows that the oxygen inhibition layer is not required for coupling of resin composites when this is performed within 2 h after polymerization of the adhesive. We speculate that although removal of the oxygen inhibition layer may eliminate the osmotic gradient that causes water migration to the adhesive-composite interface, interaction between the tertiary amine and acidic monomers may still occur even when the acidic functional groups are attached to the polymer. However, unlike free acidic monomers that are present...
in the oxygen inhibition layer, these acidic functional groups can be deleted quickly along the adhesive-composite interface as the bulk of the polymeric acids are stabilized and can only engage in localized movement. Such a hypothesis should be tested in future studies.

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REFERENCES


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