Systematic review of the chemical composition of contemporary dental adhesives

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Abstract

Dental adhesives are designed to bond composite resins to enamel and dentin. Their chemical formulation determines to a large extent their adhesive performance in clinic. Irrespective of the number of bottles, an adhesive system typically contains resin monomers, curing initiators, inhibitors or stabilizers, solvents and sometimes inorganic filler. Each one of these components has a specific function.

The aim of this article is to systematically review the ingredients commonly used in current dental adhesives as well as the properties of these ingredients. This paper includes an extensive table with the chemical formulation of contemporary dental adhesives.

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Keywords: Dental adhesive; Chemical composition; Resin; Initiator; Inhibitor; Filler

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1. Introduction

The primary aim of dental adhesives is to provide retention to composite fillings or composite cements. In addition to withstanding mechanical forces, and in particular shrinkage stress from the lining composite, a good adhesive also should be able to prevent leakage along the restoration’s margins. Clinically, failure of restorations occurs more often due to inadequate sealing, with subsequent discoloration of the cavity margins, than due to loss of retention [1,2].

The adhesive capacity of dental adhesives is based on a twofold adhesion. First, the adhesive adheres to enamel and dentin, and second, the adhesive binds the lining composite. The latter has been shown to be a process of co-polymerization between the adhesive and the lining composite, dental adhesives contain monomers that become interlocked in the retentions upon co-polymerization between the adhesive and the lining composite will provide good adhesion to the composite.

The chemical composition of adhesives is (—or at least should be—) aimed at fulfilling all above-mentioned processes. Even though dental adhesives can be classified in two main groups, i.e. etch & rinse (E&Rs) and self-etch adhesives (SEAs) (Fig. 1), they all contain similar ingredients, irrespective of the number of bottles of which an adhesive consists. Nevertheless, the proportional composition differs between the different classes of adhesives. Traditionally, adhesives contain acrylic resin monomers, organic solvents, initiators and inhibitors, and sometimes filler particles. It is self-evident that every component has a specific function. Good insights in the chemical properties of the adhesives’ components are paramount to understand or even predict their behavior.

The objective of this review article is to gather information on the properties of chemical components of which contemporary adhesives commonly consist. Regrettably, specific information about some chemical components of adhesives is scarce, like for example for the proprietary monomers. In addition, manufacturers are usually reluctant to reveal the composition of their adhesives. In order to avoid disclosure of the components, they often use descriptive terms. Unbiased research as to the composition of adhesives is also limited (or maybe not always published when performed by manufacturers themselves).

Factors related to common ingredients, such as resin, initiator, inhibitor, solvent and filler particles will be reviewed. After some general information, some specific ingredients will be discussed. Table 1 lists the chemical formulation of current dental adhesives according to the aforementioned classification, as gathered from commercial manufacturers (abbreviations Table 2).

2. Chemical composition

2.1. Resin components

In order to assure a good covalent bond between the adhesive and the lining composite, dental adhesives contain...
resin monomers that are similar to those in composite restorative materials. Similar to composites, the cured resin in the adhesive, also called the matrix, functions as a backbone providing structural continuity and thus physico-mechanical properties such as strength. Monomers should thus be considered as most important components of the adhesive. They are the key constituents of adhesives.

Basically, two kinds of monomers can be distinguished: cross-linkers and functional monomers (Fig. 2). Whereas the latter commonly have only one polymerizable group, cross-linkers have two polymerizable groups (vinyl-groups or \(-\text{C} = \text{C}\)-) or more [9]. Most functional monomers also exhibit a particular chemical group, the so-called functional group, which will impart monomer-specific functions. Functional monomers will form linear polymers upon curing, in contrast to cross-linkers that form cross-linked polymers. Compared to linear polymers, the latter have proven to exhibit better mechanical strength, and cross-linking monomers are therefore important to reinforce the adhesive resin [10–14]. Some monomers have a more intricate molecular structure, and have several polymerizable and functional groups [15]. So, they belong both to the group of functional and cross-linking monomers (for example PENTA, BPDM, TCB and PMD (Fig. 3 and Table 1) [16]. However, some of these monomers will readily hydrolyze upon admixture with water and form separate functional monomers. Typical examples are di-HEMA phosphate and pyro-EMA (DENTSPLY) that will hydrolyze to form HEMA-phosphate (Fig. 3). Traditionally, primers contained the hydrophilic functional monomers, while the hydrophobic cross-linkers were applied in a following application step (e.g.: three-step etch&rinse (3-E&R) and two step self-etch adhesives (2-SEAs) (Fig. 1). A trend towards simplification has urged manufacturers into conceiving adhesives in which both are blended (two-step etch&rinse (2-E&R) and one-step self-etch adhesives (1-SEAs)) [17].

The structure of monomers can be divided in three distinct parts: one or more polymerizable groups grafted onto a spacer, and a functional group (Fig. 2). Different kinds of polymerizable groups, and hence resin systems exist (Fig. 2). Acrylates, and especially methacrylate monomers are most common. In general, the advantages of acrylic systems are an easy radical polymerization reaction, and their colorless and tasteless character [14]. The main difference between acrylates and methacrylates (one additional methylgroup) is their reactivity. In contrast to methacrylates, the double bonds of acrylates are much more reactive and may therefore pose biocompatibility and shelf-life problems [18]. Moreover, methacrylates are also less sensitive to oxygen inhibition [19]. Both acrylates and methacrylates are vulnerable to water degradation (hydrolysis) of the ester group (\(\text{R}_1\text{C} = \text{O} - \text{OR}_2\)) [20]. A new group of monomers, methacrylamides, was designed to overcome these problems (Fig. 2). Methacrylamides have an amide group (\(\text{R}_1\text{C} = \text{O} - \text{NH} - \text{R}_2\)) instead of an ester group, which is more resistant to water [21–23]. Considering polarity, the polymerizable group generally exhibits hydrophobic behavior.
Table 1
The chemical composition of currently available adhesive systems

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>pH</th>
<th>Remarks</th>
<th>Dry or wet bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-step etch&amp;rinse adhesives (3-E&amp;R)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Adper Scotchbond Multi-Purpose</td>
<td>3M ESPE, St Paul, MN, USA</td>
<td>Component 1 (etchant): 35% H₃PO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Component 2: Scotchbond Multi-Purpose primer HEMA, polyalkenoic acid polymer, water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Component 3: Scotchbond Multi-Purpose (both for light-cure and self-cure initiators), photo-initiator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adper Scotchbond Multi-Purpose Plus</td>
<td>3M ESPE, St Paul, MN, USA</td>
<td>Component 1 (etchant): 35% H₃PO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Component 1,5: Scotchbond Multi-Purpose Plus activator ethanol, sulfonic acid salt, sodium salt</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>Component 2: Scotchbond Multi-Purpose primer HEMA, polyalkenoic acid polymer, water</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Component 3: Scotchbond Multi-Purpose (both for light-cure and self-cure initiators), photo-initiator</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Component 3,5: Scotchbond Multi-Purpose Plus catalyst Bis-GMA, HEMA, BPO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All-Bond 2</td>
<td>Bisco Inc, Schaumburg, IL, USA</td>
<td>Etchant: 10% H₃PO₄ (All-etch) or 32% H₃PO₄ (Uni-etch)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Primer A: NTG-GMA, acetone, ethanol, water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond-it</td>
<td>Pentron Corporation, Wallingford, CT, USA</td>
<td>Etchant: 37% H₃PO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Primer A: NTG-GMA, acetone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Primer B: PMGDMD, Bis-GMA, HEMA, acetone, photo-initiator</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Adhesive resin: Bis-GMA, HEMA, UDMA, HDDMA with amine accelerator, photo-initiator, BPO</td>
<td></td>
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</tr>
<tr>
<td>Clearfil Liner Bond</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td>Etchant: K-etchant</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>SA primer: 5-NMSA, ethanol, water</td>
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<td></td>
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<td>Photo bond:</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Catalyst liquid: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, BPO, CQ</td>
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<tr>
<td></td>
<td></td>
<td>Universal liquid: N,N’-diethanol p-toluidine, sodium benzen sulfinate, ethanol</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ecosit-Primer/Mono</td>
<td>DMG, Hamburg, Germany</td>
<td>Ecosit-Etch: 37% H₃PO₄</td>
<td>2.6</td>
<td>Light cure</td>
<td>Preferentially moist</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Primer: maleic acid, HEMA, polymethacrylated polycarboxylic acid Bonding: Bis-GMA, TEGDMA, polymethacrylated oligomaleic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FL bond (Imperva Fluorobond in Japan)</td>
<td>Shofu Inc., Kyoto, Japan</td>
<td>Etchant: 7% H₃PO₄</td>
<td>2.2</td>
<td>Fluoride releasing Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Primer A: water, acetone, initiator</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Primer B: 4-AET, 4-AETA, HEMA, UDMA, TEGDMA, initiator</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Bond: F-PRG Filler, HEMA, UDMA, TEGDMA, photo-initiator</td>
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</tr>
<tr>
<td>Gluma Solid Bond</td>
<td></td>
<td>Gluma Etch: 20–35% H₃PO₄</td>
<td>1.8</td>
<td>Light cure</td>
<td>Wet</td>
</tr>
<tr>
<td>Adhesive</td>
<td>Manufacturer</td>
<td>Composition</td>
<td>pH</td>
<td>Remarks</td>
<td></td>
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</tr>
</tbody>
</table>
| Optibond | Kerr, Orange, CA, USA | *Etchant:* 37.5% H$_3$PO$_4$  
*FL Prime:* HEMA, GPDM, MMEP, water, ethanol, CQ, BHT  
*FL Adhesive:* Bis-GMA, HEMA, GDMA, CQ, ODMAB, filler (fumed SiO$_2$, barium aluminoborosilicate, barium aluminosilicate, Na$_2$SiF$_6$), coupling factor A174 | FL Prime: 1.9  
FL Adhesive: 6.9 | Light cure |
| Optibond FL | Kerr, Orange, CA, USA | *Etchant:* 37.5% H$_3$PO$_4$  
*FL Primer:* HEMA, GPDM, MMEP, water, ethanol, CQ, BHT  
*FL Adhesive:* Bis-GMA, HEMA, GDMA, CQ, ODMAB, filler (fumed SiO$_2$, barium aluminoborosilicate, barium aluminosilicate, Na$_2$SiF$_6$), coupling factor A174 (approximately 48 wt% filled) | Primer: 3.5  
Bonding: 5 | Wet |
| PAAMA | SDI limited, Bayswater, Victoria, Australia | *Etchant:* 37% H$_3$PO$_4$  
*Primer:* acetone, proprietary hydrophilic/hydrophobic monomer, TEGDMA  
*Bonding:* UDMA, TEGDMA, stabilizers, CQ | | |
| Probond | DENTSPLY Caulk, Milford, DE, USA | *Etchant:* H$_3$PO$_4$  
*Primer:* PENTA, acetone, ethanol, stabilizers  
*Adhesive:* PENTA, UDMA, methacrylate monomers, glutaraldehyde, CQ, stabilizers | | Wet |
| Quadrant Unibond | Cavex Holland B.V., Haarlem, the Netherlands | *Quadrant total-etch:* 20% H$_3$PO$_4$  
*Primer:* HEMA, TEGDMA, maleic acid, polycarboxylic acid, ethanol, water, CQ  
*Bonding:* Bis-GMA, TEGDMA, silicate glass fillers, silica, polycarboxylic acid, CQ | | Light cure |
| Solobond Plus | VOCO, Cuxhaven, Germany | *Etchant:* Vococid 35% H$_3$PO$_4$  
*Primer:* water, acetone, hydroxymethacrylate fluorides, acidic monomers, maleic acid  
*Adhesive:* acetone, BIS-GMA, TEGDMA, hydroxymethacrylate, CQ | Primer: 2.4  
Adhesive: 5.8 | Wet |
| Syntac | Ivoclar Vivadent, Schaan, Liechtenstein | *Total Etch:* 37% H$_3$PO$_4$  
*Primer:* TEGDMA, PEGDMA, maleic acid, dimethylketon, water  
*Adhesive:* PEGDMA, glutaraldehyde, water | | Light cure |
| Two-step etch&rinse adhesive (2-E&R) | | | | |
| Adper Scotchbond 1 XT Adhesive (also Single Bond) | 3M ESPE, St Paul, USA | *Etchant:* 35% H$_3$PO$_4$  
*Adhesive:* dimethacrylates, HEMA, polyalkenoid acid copolymer, 5 nm silane treated colloidal silica, ethanol, water, photo-initiator | | Light cure |
| Bond-1 | Pentron Corporation, Wallingford, CT, USA | *Etchant:* 37% H$_3$PO$_4$  
*Adhesive:* PMGDM, HEMA, TMPTMA, initiators, acetone | | Light cure |
<p>| Clearfil Photobond | | <em>K-etchant</em> | | Dual cure |</p>
<table>
<thead>
<tr>
<th>Adhesive Manufacturer</th>
<th>Composition</th>
<th>pH</th>
<th>Remarks</th>
<th>Dry or wet bonding</th>
</tr>
</thead>
</table>
| Kuraray Medical Inc, Tokyo, Japan | **Catalyst liquid**: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, BPO, CQ  
**Universal liquid**: N,N-diethanol p-toluidine, sodium benzen sulfinate, ethanol |  |  |  |
| Clearfil New Bond Kuraray Medical Inc, Tokyo, Japan | K-etchant  
**Catalyst liquid**: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, BPO  
**Universal liquid**: N,N-diethanol p-toluidine, sodium benzen sulfinate, ethanol |  | Self-cure |  |
| Excite Ivoclar Vivadent, Schaan, Liechtenstein | **Total Etch**: 37% H$_3$PO$_4$  
**Adhesive**: HEMA, phosphonic acid acrylate, Bis-GMA, dimethacrylates, silica, ethanol, catalysts, stabilizers | 2.8 | Light cure | Wet |
| Excite DSC Ivoclar Vivadent, Schaan, Liechtenstein | **Total Etch**: 37% H$_3$PO$_4$  
**Adhesive**: HEMA, phosphonic acid acrylate, dimethacrylates, silica, ethanol, catalysts, stabilizers  
**Microbrush**: layered with initiators |  | Dual cure |  |
| Gluma Comfort Bond Heraeus Kulzer, Hanau, Germany | **Gluma Etch**: 20–35% H$_3$PO$_4$  
**Adhesive**: UDMA, HEMA, 4-META, modified polyacrylic acid, ethanol, water, photo-initiators, stabilizers | 2.8 | Light cure | Wet |
| Gluma One Bond Heraeus Kulzer, Hanau, Germany | **Gluma Etch**: 20–35% H$_3$PO$_4$  
**Adhesive**: UDMA, HEMA, 4-META, acetone, photo-initiators, stabilizers |  | Light cure | Wet |
| Heliobond Ivoclar Vivadent, Schaan, Liechtenstein | **Total Etch etchant**: 37% H$_3$PO$_4$  
**Adhesive**: Bis-GMA, TEGDMA, catalysts, stabilizers |  | Dry |  |
| One Coat Bond Coltene-Whaledent, Altstätten, Switzerland | **Etchant**: Coltene etchant 15 (15% H$_3$PO$_4$) or Coltene etchant gel s (35% H$_3$PO$_4$)  
**Adhesive**: HEMA, HPMA, glycerol dimethacrylate, methacrylated polyalkenoate, UDMA, amorphous silica, CQ |  | Light cure | Wet |
| One-Step Bisco Inc, Schaumburg, IL, USA | **Etchant**: 32% H$_3$PO$_4$ (Uni-etch), 37% H$_3$PO$_4$ (Etch-37) or Tyrian SPE  
**Adhesive**: BPDM, Bis-GMA, HEMA, acetone, photo-initiator |  | Light cure | Wet |
| One-Step Plus Bisco Inc, Schaumburg, IL, USA | **Etchant**: 32% H$_3$PO$_4$ (Uni-etch), 37% H$_3$PO$_4$ (Etch-37) or Tyrian SPE  
**Adhesive**: BPDM, Bis-GMA, HEMA, acetone, photo-initiator, 8.5 wt% fluoroaluminosilicate glass fillers (proprietary fillers) (1 μm) |  | Light cure | Wet |
| Optibond Solo Plus Kerr, Orange, CA, USA | **Etchant**: 37.5% H$_3$PO$_4$  
**Adhesive**: Bis-GMA, HEMA, GDMA, GPDM, ethanol, CQ, ODMAB, BHT, filler (fumed SiO$_2$, barium aluminoborosilicate, Na$_2$SiF$_6$), coupling factor A174 (approximately 15 wt% filled) |  | Light cure |  |
| Optibond Solo Plus Dual cure Kerr, Orange, CA, USA | **Etchant and adhesive**: (see above)  
**Activator**: Bis-GMA, HEMA, ethanol, DHEPT, BS acid |  | Dual cure |  |
| Polibond VOCO, Cuxhaven, Germany | **Etchant**: Vococid 35% H$_3$PO$_4$  
**Bottle A+B**: Bis-GMA, TEGDMA, hexandioldimethacrylate, BPO | 6.9 |  | Enamel adhesive |
Table 1 (continued)

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>pH</th>
<th>Remarks</th>
<th>Dry or wet bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prime&amp;Bond NT</td>
<td>DENTSPLY</td>
<td><em>Etchant:</em> H₃PO₄, <em>Adhesive:</em> PENTA, TEGDMA, Bis-GMA, cetylamine hydrofluoride, acetone, nanofiller (amorphous silicon dioxide 8 nm), resin R5-62-1, T-resin, D-resin, CQ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prime&amp;Bond NT dual cure</td>
<td>DENTSPLY Caulk</td>
<td><em>Self-cure activator:</em> aromatic sodium sulfinate, acetone, ethanol</td>
<td></td>
<td>Dry or wet bonding is needed. Needs to be mixed with Prime&amp;Bond NT</td>
<td></td>
</tr>
<tr>
<td>Quadrant Uni-1-Bond</td>
<td>Cavex Holland B.V., Haarlem, the Netherlands</td>
<td><em>Quadrant Total-Etch:</em> 20% H₃PO₄, <em>Adhesive:</em> 4-META, Bis-GMA, HEMA, UDMA, maleic acid, polyacrylic acid, ethanol, water, CQ</td>
<td></td>
<td></td>
<td>Dry &amp; wet</td>
</tr>
<tr>
<td>Solist</td>
<td>DMG, Hamburg, Germany</td>
<td><em>Ecosit-Etch:</em> 37% H₃PO₄, <em>Adhesive:</em> HEMA, TEGDMA, elastomers, methacrylated phosphoric acid</td>
<td>2.2</td>
<td></td>
<td>Wet</td>
</tr>
<tr>
<td>Solobond M</td>
<td>VOCO, Cuxhaven, Germany</td>
<td><em>Etchant:</em> Vococid 35% H₃PO₄, <em>Adhesive:</em> BIS-GMA, HEMA, phosphate methacrylates, BHT, acetone, CQ, amine accelerator</td>
<td>2.2</td>
<td></td>
<td>Wet</td>
</tr>
<tr>
<td>Stae</td>
<td>SDI limited, Bayswater, Victoria, Australia</td>
<td><em>Etchant:</em> 37% H₃PO₄, <em>Adhesive:</em> acetone, water, proprietary hydrophilic/hydrophobic monomer, HEMA, CQ, stabilizer</td>
<td>3.5</td>
<td>Light cure</td>
<td>Wet</td>
</tr>
<tr>
<td>Superbond C&amp;B</td>
<td>Sun Medical Co, Shiga, Japan</td>
<td><em>Red activator (for enamel):</em> aqueous phosphoric acid, organic thickener</td>
<td>2.1</td>
<td>Red Activator: 1</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Green activator (for dentin):</em> aqueous citric acid, ferric chloride</td>
<td></td>
<td>Green Activator: 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Monomer:</em> 4-META, MMA</td>
<td></td>
<td>Cement mixture: 6</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td><em>Catalyst:</em> partially oxidized tributylborane (TBB)</td>
<td></td>
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<td><em>Polymer (clear):</em> polymethylmethacrylate</td>
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<tr>
<td>XPBOND</td>
<td>DENTSPLY</td>
<td>*PENTA, TCB, HEMA, TEGDMA, UDMA, tert-butanol, nanofiller, CQ, stabilizer</td>
<td>~2.1</td>
<td></td>
<td>Wet</td>
</tr>
<tr>
<td>2-step self-etch adhesive (2-SEA)</td>
<td></td>
<td><em>Ivoelar:</em> acrylic ether phosphonic acid, bisacrylamide, water, CQ, stabilizers</td>
<td></td>
<td>Primer: 1.7</td>
<td>Light cure</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Vivadent:</em> Bis-GMA, GDMA, HEMA, fumed silica, CQ, tertiary amine, stabilizers</td>
<td></td>
<td>Bonding: 7.7</td>
<td></td>
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<tr>
<td>Clearfil Liner Bond 2</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td><em>Primer A:</em> Phenyl-P, 5-NMSA, CQ, ethanol</td>
<td></td>
<td>Mixed primer: 1.4</td>
<td>Light cure</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Primer B:</em> HEMA, water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clearfil Liner Bond II in Japan</td>
<td></td>
<td><em>LB BOND:</em> MDP, HEMA, hydrophobic dimethacrylate, CQ, silanated colloidal silica</td>
<td></td>
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</tr>
<tr>
<td>Clearfil Liner Bond 2V</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td><em>Primer A:</em> MDP, HEMA, hydrophilic dimethacrylate, N-N-diethanol p-toluidine, photo-initiator, water</td>
<td></td>
<td>Mixed primer: 2.8</td>
<td>Dual cure</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Primer B:</em> HEMA, hydrophilic dimethacrylate, water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Bond A:</em> MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, CQ, silanated colloidal silica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Bond B:</em> HEMA, Bis-GMA, hydrophilic dimethacrylate, BPO, N,N-diethanol p-toluidine, CQ, silanated colloidal silica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesive</td>
<td>Manufacturer</td>
<td>Composition</td>
<td>pH</td>
<td>Remarks</td>
<td>Dry or wet bonding</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>----------</td>
<td>------------------------------------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Clearfil Protect Bond</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td>Primer: MDPB, MDP, HEMA, hydrophilic dimethacrylate, photo-initiator, water</td>
<td>2</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td>Clearfil SE Bond</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td>Primer: MDP, HEMA, hydrophilic dimethacrylate, photo-initiator, water</td>
<td>2</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td>Clearfil Mega Bond in Japan</td>
<td>DMG, Hamburg, Germany</td>
<td>Primer: Maleic acid, water</td>
<td>2.6; 1.3 in water</td>
<td>An optional activator (contains BPO as active ingredient) is available to ensure compatibility with dual cure and chemical cure materials. However, Contax still needs to be light cured</td>
<td>Preferentially moist</td>
</tr>
<tr>
<td>Nano-Bond</td>
<td>Pentron Corporation, Wallingford, CT, USA</td>
<td>Self-etch primer: sulfonic acid terminated resin, HEMA, water</td>
<td></td>
<td></td>
<td>Light cure or dual cure when activator is added</td>
</tr>
<tr>
<td>One Coat Self Etching Bond</td>
<td>Coltene-Whaledent, Altstätten, Switzerland</td>
<td>Primer: water, HEMA, acrylamidosulfonic acid, glycerol mono- and dimethacrylate, methacrylated polyalkenoate</td>
<td></td>
<td></td>
<td>Light cure</td>
</tr>
<tr>
<td>Optibond Solo Plus Self-etch</td>
<td>Kerr, Orange, CA, USA</td>
<td>Self-etch primer: HFGA-GMA, GPDM, ethanol, water, MEHQ, ODMAB, CQ</td>
<td>SE primer: 1.9</td>
<td>Adhesive: 2.2</td>
<td>Light cure</td>
</tr>
<tr>
<td>Tokuso Mac Bond II</td>
<td>Tokuyama Dental Corporation, Tokyo, Japan</td>
<td>Self-etch primer (primer a+primer b): MAC-10, methacryloylalkyl acid phosphate, water, acetone</td>
<td></td>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>Unifil Bond</td>
<td>GC, Tokyo, Japan</td>
<td>Primer: 4-MET, HEMA, ethanol, water, CQ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-step self-etch adhesive (1-SEA)</td>
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<td>Bonding: UDMA, HEMA, DMA, CQ, silica</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Absolute</td>
<td>DENTSPLY Sankin Kogyo, Otahara, Japan</td>
<td>Methacrylate ester, fluoride compound, anhydrous silicic acid, acetone</td>
<td>Does not contain water</td>
<td>Does not contain water</td>
<td>Wet</td>
</tr>
<tr>
<td>Admira Bond</td>
<td>VOCO, Cuxhaven, Germany</td>
<td>Ormocers, BIS-GMA, HEMA, phosphate methacrylates, BHT, acetone, CQ, amine accelerator</td>
<td>2.1</td>
<td></td>
<td>Wet</td>
</tr>
<tr>
<td>Adper Prompt L Pop</td>
<td>3 M ESPE, ST Paul, USA</td>
<td>Red cushion: Methacrylic phosphates, BIS-GMA, photo-initiator</td>
<td>Light cure</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yellow cushion: Water, HEMA, polyalkenoic acid polymer</td>
<td></td>
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</table>
Table 1 (continued)

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>pH</th>
<th>Remarks</th>
<th>Dry or wet bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQ Bond</td>
<td>Sun Medical Co, Shiga, Japan</td>
<td>AQ Bond: water, acetone, 4-META, UDMA, monomethacrylates, photo-initiator, stabilizer</td>
<td>2.5</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AQ sponge: sodium p-toluene sulfinate adsorbed in polyurethane foam</td>
<td></td>
<td>Contains special ternary catalysts to enhance coupling with chemically cured resins</td>
<td></td>
</tr>
<tr>
<td>Clearfil S Bond</td>
<td>Kuraray Medical Inc, Tokyo, Japan</td>
<td>MDP, Bis-GMA, HEMA, photo-initiators, ethanol, water, silanated colloidal silica</td>
<td>2.7</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td>Futurabond NR</td>
<td>VOCO, Cuxhaven, Germany</td>
<td>Bottle A and B: BIS-GMA, HEMA, phosphate methacrylates, BHT, ethanol, fluorides, CQ, silicium dioxide nanoparticles</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-Bond</td>
<td>GC, Tokyo, Japan</td>
<td>4-MET, phosphoric ester-monomer, UDMA, TEGDMA, acetone, water, stabilizer, silica filler, water, photo-initiator</td>
<td>2</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td>Hybrid Bond</td>
<td>Sun Medical Co, Shiga, Japan</td>
<td>Hybrid base: water, acetone, 4-META, polyfunctional acrylate, monomethacrylates, photo-initiators, stabilizer Hybrid brush: sodium p-toluene sulfinate and aromatic amine adsorbed on the brush hairs</td>
<td>2.5</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td>iBond</td>
<td>Heraeus Kulzer, Hanau, Germany</td>
<td>UDMA, 4-META, glutaraldehyde, acetone, water, photo-initiators, stabilizers</td>
<td>2</td>
<td>Light cure Contains glutaraldehyde</td>
<td>Dry</td>
</tr>
<tr>
<td>One-up F Bond</td>
<td>Tokuyama Dental Corporation, Tokyo, Japan</td>
<td>Bonding Agent A: MAC-10, photo-initiator, methacryloylalkyl acid phosphate, multifunctional methacrylic monomers Bonding Agent B: MMA, HEMA, water, F-deliverable micro-filler (fluoro-alumino-silicate glass), photo-initiator</td>
<td>Bonding agent A:0.3 Bonding agent B:8.0 Mixture:1.2</td>
<td>Light cure</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bonding agent A: MAC-10, photo-initiator, methacryloylalkyl acid phosphate, multifunctional methacrylic monomer Bonding agent B: MMA, HEMA, water, F-deliverable micro-filler (fluoro-alumino-silicate glass), photo-initiator</td>
<td>Bonding agent A:0.7 Bonding agent B:7.7 Mixture:1.2</td>
<td>In addition to the above features for One-up F Bond, less technical sensitivity is featured</td>
<td>Dry and moist</td>
</tr>
<tr>
<td>Reactmer Bond</td>
<td>Shofu Inc, Kyoto, Japan</td>
<td>Bond A: F-PRG filler, fluoro-alumino silicate glass, water, acetone, initiator</td>
<td>2.6</td>
<td>Fluoride releasing</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bond B: 4-AET, 4-AETA, HEMA, UDMA, photo-initiator</td>
<td></td>
<td>Light cure</td>
<td></td>
</tr>
<tr>
<td>Tyrian SPE</td>
<td>Bisco Inc, Schaumburg, IL, USA</td>
<td>Primer A: thymol blue, ethanol, water</td>
<td></td>
<td>Color indicator</td>
<td>Dry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Primer B: AMPS, BidMEP (Bis[2-ethyl]phosphate), TPO, ethanol</td>
<td></td>
<td>Can be used as self-etching primer together with All-Bond2, One-Step and One Step Plus</td>
<td></td>
</tr>
<tr>
<td>Unicem</td>
<td>3 M ESPE, ST Paul, MN, USA</td>
<td>Liquid: methacrylated phosphoric acid ester, dimethacrylates, photo-initiator, stabilizer Powder: glasspowder, silica, calcium hydroxide, initiator, pigment, polymer</td>
<td></td>
<td></td>
<td>Dual cure</td>
</tr>
<tr>
<td>Xeno III (Xeno CF II in Japan)</td>
<td>DENTSPLY De Trey, Konstanz, Germany</td>
<td>Bottle A: HEMA, ethanol, water, aerosil, stabilizers (BHT)</td>
<td>&lt;1</td>
<td></td>
<td>Dry</td>
</tr>
</tbody>
</table>
The spacer of the monomer does not have a function as such, except for keeping both functional and polymerizable groups well separated, but it has an important influence on the properties of the monomer and the resulting polymer [24]. The spacer is usually an alkyl chain, but can also contain several other groups, like esters, amides, or aromatic groups. The polarity of the spacer will partly determine the solubility of the monomer in water, and in other solvents. The hydrophilicity of the spacer group may also cause water uptake, which leads to higher hydrolysis susceptibility of the monomers as well as swelling and discoloration of the cured resin. The size of the spacer group determines the viscosity of the monomers, and as a consequence also their wetting and penetration behavior. In addition, small monomers will be more volatile than larger molecules [18]. The spacer also influences the flexibility of the monomer. Moreover, stereochemic and substituent effects by the spacer will modify the reactivity of polymerizable and/or functional groups [14]. Voluminous groups may cause other monomers not to reach the polymerizable group, thereby hindering good polymerization (steric hindering) [14]. It was shown in homopolymerization studies that the reactivity of monomers increases with increasing distance between the methacrylate groups [18] and the flexibility of the spacer of the monomer [25].

The functional group in functional monomers usually exhibits hydrophilic properties. This group may serve several purposes: enhancing wetting and demineralization of dentin, but also releasing fluoride or imparting the monomer antibacterial properties. So-called adhesion-promoting functional monomers self-evidently enhance bond strength of adhesives to dentin by their hydrophilic properties [26]. The most common functional groups used in commercial monomers are phosphate, carboxylic acid and alcohol groups (Figs. 2 and 3). Sulfonic acid, phosphate, phosphonate and carboxyl groups will dissociate to release protons in aqueous solutions, and will be able to react in acid–base reactions. Apart from ‘adhesion-promoting’ or wetting effects, these proton-releasing functional groups may establish surface demineralization to a certain extent when applied in a sufficient concentration. A ranking on etching aggressiveness can be made according to the acidity of these groups: sulfonic acid > phosphonic > phosphoric > carboxylic acid > alcohol [21,22]. Dihydrogen acids are always more acidic than their monohydrogen counterparts, as they can dissociate to form more protons [27]. Sometimes, very particular functional groups can be built into a monomer. PEM-F (DENTSPLY) (Fig. 3) is a monomer with 5 methacrylate-alkyl chains grafted onto a ring structure (cyclophosphazene), onto which also a fluoride as a functional group is grafted. The rationale for this monomer is the release of fluoride upon admixture with water, which will scavenge calcium in order to intensify the demineralization reaction, and not to release fluoride. NPG-GMA and NTG-GMA (Fig. 3) are adhesion-promoting monomers that also function as co-initiator due to their tertiary aromatic amine group [28]. DMAEMA (Fig. 3) is a water-soluble monomer that has a tertiary amino moiety also functioning as a co-initiator for camphorquinone [29]. As these molecules will be fixed in the polymer network upon curing, good biocompatibility is assured. MDPB (Fig. 3), a monomer patented by Kuraray, is a compound of the antibacterial agent dodecylpyridinium bromide and a methacryl group [30]. In contrast to the majority of functional monomers, this molecule is rather hydrophobic. 5-NMSA, a monomer used in former adhesives of Kuraray and in Panavia cements, has a salicyl group that is intended to chelate with calcium in order to obtain a desensitizing effect.

Depending on several factors, such as hydrophilic behavior, methacrylate monomers are susceptible to hydrolysis in aqueous solutions. Not only the ester-group typical of acrylates can hydrolyze, but also phosphate and carboxyl groups used in functional monomers may be vulnerable to hydrolysis in water (Fig. 4).

The conversion rate is an important determinant of the physico-mechanical strength of the resulting polymer [14,31,32]. Conversion is seldom complete and is generally accepted to be rather low in dental composites and adhesives [33,34]. Especially in simplified adhesives the degree of conversion was shown to be low [35,36]. Apart from low mechanical strength, low conversion rate also results in higher permeability [36], more water

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>pH</th>
<th>Remarks</th>
<th>Dry or wet bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xeno IV</td>
<td>DENTSPLY Sankin Kogyo, Otahara, Japan</td>
<td>Bottle B: Pyro-EMA, PEM-F, UDMA, CQ, BHT, ethyl-4-dimethylaminobenzoate (co-initiator)</td>
<td>~2.1</td>
<td></td>
<td>Dry</td>
</tr>
</tbody>
</table>

Data provided by the manufacturer. The adhesives are categorized according to the classification of Van Meerbeek [5]. Abbreviations: see Table 2.
sorption [37], more nanoleakage [38], degradation of the tooth-composite bond [39] and more leaching of residual uncured monomers and thus lower biocompatibility of dental adhesives. Polymerization is inhibited by several factors, such as the presence of oxygen (resulting in the oxygen-inhibition layer) [40,41], the presence of intrinsic 

### Table 2

**Abbreviations of monomers, initiators and inhibitors, filler particles and coupling factors used in adhesives**

#### Abbreviations monomers

<table>
<thead>
<tr>
<th>Monomer Abbreviation</th>
<th>Monomer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-AETA</td>
<td>4-acryloyloxyethyl trimellitate anhydride</td>
</tr>
<tr>
<td>4-AET</td>
<td>4-acryloyethyl trimellitic acid</td>
</tr>
<tr>
<td>AMPS</td>
<td>2-acrylamido-2-methyl-1-propanesulfonic acid</td>
</tr>
<tr>
<td>Bis-MEP</td>
<td>bis[2-(methacryloyloxy)ethyl] phosphate</td>
</tr>
<tr>
<td>Bis-EMA</td>
<td>ethoxylated bisphenol A glycol dimethacrylate</td>
</tr>
<tr>
<td>Bis-GMA</td>
<td>bisphenol A diglycidyl methacrylate</td>
</tr>
<tr>
<td>BPDM</td>
<td>biphenyl dimethacrylate or 4,4'-dimethacryloxyethoxybenziliphenyl-3,3'-dicarboxylic acid</td>
</tr>
<tr>
<td>Di-HEMA</td>
<td>di-2-hydroxyethyl methacryl hydrogenphosphate</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>dimethylaminoethyl methacrylate</td>
</tr>
<tr>
<td>EAEPA</td>
<td>ethyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate</td>
</tr>
<tr>
<td>EGDMA</td>
<td>ethyleneglycol dimethacrylate</td>
</tr>
<tr>
<td>GDMA</td>
<td>glycerol dimethacrylate</td>
</tr>
<tr>
<td>GPDM</td>
<td>glycerol phosphate dimethacrylate</td>
</tr>
<tr>
<td>HDDMA</td>
<td>1,6-hexanediol dimethacrylate</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-hydroxymethyl methacrylate</td>
</tr>
<tr>
<td>HEMA-phosphate</td>
<td>2-hydroxethyl methacryl dihydrogenphosphate</td>
</tr>
<tr>
<td>HFGA-GMA</td>
<td>hexafluorogluaric anhydr degrade-cleidometacrylate adduct</td>
</tr>
<tr>
<td>HPMA</td>
<td>2-hydroxypropyl methacrylate</td>
</tr>
<tr>
<td>MA</td>
<td>methacrylic acid</td>
</tr>
<tr>
<td>MAEPA</td>
<td>2,4,6 trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate</td>
</tr>
<tr>
<td>MAC-10</td>
<td>11-methacryloyloxy-1,1'-undecanedicarboxylic acid</td>
</tr>
<tr>
<td>10-MDP</td>
<td>10-methacryloyloxydecyl dihydrogenphosphate</td>
</tr>
<tr>
<td>MDPP</td>
<td>methacryloyloxydodecyldipropynium bromide</td>
</tr>
<tr>
<td>4-META</td>
<td>4-methacryloyloxyethyl trimellitate anhydride</td>
</tr>
<tr>
<td>4-MET</td>
<td>4-methacryloyloxyethyl trimellitic acid</td>
</tr>
<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>MMEP</td>
<td>mono-2-methacryloyloxyethyl phthalate (sometimes also called PAMA: phthalic acid monomethacrylate)</td>
</tr>
<tr>
<td>5-NMSA</td>
<td>5-methacryloyloxy-5-aminosalicylic acid</td>
</tr>
<tr>
<td>NPG-GMA</td>
<td>N-phenylglycine glycyl methacrylate</td>
</tr>
<tr>
<td>NTG-GMA</td>
<td>N-tolylglycine glycidyl methacrylate or N-(2-hydroxy-3-((2-methyl-1-oxo-2-propenyl)oxy)propyl)-N-tolyl glycine</td>
</tr>
<tr>
<td>PEGDMA</td>
<td>polyethylene glycol dimethacrylate</td>
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<tr>
<td>PEM-F</td>
<td>pentamethacryloyloxyethylhexahexaphosphazene monofluoride</td>
</tr>
<tr>
<td>PENTA</td>
<td>dipentaerythritol pentaacrylate monophosphate</td>
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<tr>
<td>Phenyl-P</td>
<td>2-(methacryloxymethoxy)phenyl hydrogenphosphate</td>
</tr>
<tr>
<td>PMDMP</td>
<td>pyromellitic diethyloxetacrylate or 2,5-dimethacryloyloxyethoxycarboxyl-1,4-benzenedicarboxylic acid</td>
</tr>
<tr>
<td>PMGDMP</td>
<td>pyromellitic glycerol dimethacrylate or 2,5-bis(1,3-dimethacryloyloxyprop-2-oxycarboxyl)benzene-1,4-dicarboxylic acid</td>
</tr>
<tr>
<td>Pyro-EMA</td>
<td>tetramethacryloyloxyethyl pyrophosphate</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>triethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>trimethylolpropane trimethacrylate</td>
</tr>
<tr>
<td>UDMA</td>
<td>urethane dimethylacrylate or 1,6-di(methacryloyloxyethylcarbamoy)-3,3',5-trimethylhexaan</td>
</tr>
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</table>

#### Abbreviations initiators and inhibitors

<table>
<thead>
<tr>
<th>Initiator Abbreviation</th>
<th>Initiator Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHT</td>
<td>butylhydroxytoluene or butylated hydroxytoluene or ,2,6-di-(tert-butyl)-4-methylphenol (inhibitor)</td>
</tr>
<tr>
<td>BPO</td>
<td>benzoylperoxide (redox initiator)</td>
</tr>
<tr>
<td>BS acid</td>
<td>benzenesulfonic acid sodium salt (redox inhibitor)</td>
</tr>
<tr>
<td>CQ</td>
<td>camphorquinone or camphoroquinone or 1.7.7-trimethylbicyclo-[2,2,1]-hepta-2,3-dione (photo-initiator)</td>
</tr>
<tr>
<td>DHEPT</td>
<td>1,3-di-(2-hydroxyethyl)-4-toluuidine (co-initiator)</td>
</tr>
<tr>
<td>MEHQ</td>
<td>4-methoxyphenol or monoethyl ether hydroquinone (inhibitor)</td>
</tr>
<tr>
<td>ODMAB</td>
<td>2-(ethylhexyl)-4-(dimethyamino)benzoate (co-initiator)</td>
</tr>
<tr>
<td>TPO</td>
<td>Lucirin TPO, BASF (photo-initiator)</td>
</tr>
<tr>
<td>UV-9</td>
<td>2-hydroxy-4-methoxybenzophenone (photo-initiator)</td>
</tr>
</tbody>
</table>

#### Abbreviations fillers and silane coupling factors

<table>
<thead>
<tr>
<th>Coupling Factor Abbreviation</th>
<th>Coupling Factor Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A174</td>
<td>γ-methacryloxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>F-PRG</td>
<td>full reaction type pre-reacted glass-ionomer fillers</td>
</tr>
<tr>
<td>NaF</td>
<td>sodium fluoride</td>
</tr>
<tr>
<td>Na2SiF6</td>
<td>disodium hexafluorosilicate</td>
</tr>
<tr>
<td>POSS nano-particulates</td>
<td>polyhedral oligomer silsesquioxanes</td>
</tr>
</tbody>
</table>
water from dentin and the presence of residual solvents in the adhesive [42,43].

Volumetric shrinkage and resulting shrinkage stresses are inherent to polymerization reactions as the intermolecular distance between the monomers is replaced by a covalent bond [14].

VOCO (Germany) replaced a certain amount of conventional resin in some composite filling materials and adhesives (Table 1) by a specific sort of polymer called ormoscer (organically modified ceramics). These polymers have a polymerized backbone of SiO₂ with methacrylate sidebranches. The latter ensure cross-linking with conventional resin compounds. The constitution and the properties of the ‘ormocer’ polymer can be modified by changing individual units. Main advantages are said to be lower shrinkage and toxicity [44].

Recently, the biocompatibility of resin monomers has come under extensive scrutiny. Several studies showed that residual monomers may dilute into saliva after curing and that degradation of resin may lead to further release of monomers into the oral environment [45]. Many monomers, especially dimethacrylates have been shown to exert cytotoxic effects [46,47]. Besides cytotoxicity, possible endocrine-disruptive effects of monomers have raised some concern [48,49].
Fig. 3. Chemical structure of monomers used in contemporary adhesive systems. Left are typical functional monomers, and on the right, cross-linking monomers are shown. In the center, some monomers with several polymerizable groups are shown, that also exhibit at least one functional group. Some of them however will dissociate in aqueous solutions to form monomers with one polymerizable group. Abbreviations: see Table 2.
The way monomers are named is most confusing. Apart from the full chemical name, an acronym or trade name is very popular. Sometimes, several synonyms exist for the same monomer. For example, hydroxyethyl methacrylate (HEMA) has many chemical synonyms, like ethylene glycol methacrylate; 2-(methacryloyloxy) ethanol; 2-methyl-2-propenoic acid 2-hydroxyethyl ester; 2-methyl-, 2-hydroxyethyl ester methacrylic acid; 2-hydroxyethyl ester; hydroxyethyl methacrylate; ethylene glycol monomethacrylate; glycol methacrylate; glycol monomethacrylate; 2-HEMA.

Research as to the properties and the effectiveness of monomers used in dental adhesive systems is remarkably scarce. Whereas composite filling materials are mostly composed of monomers that have been amply researched such as Bis-GMA, TEGDMA and UDMA, adhesives also contain rather ‘unknown’ monomers. Several manufacturers have started synthesizing proprietary monomers, which they protect by patents. It is self-evident that active patents may also hinder objective research. Moreover, only a study set-up with experimental adhesives with different amounts of one single component can truly investigate the role of an ingredient. Most studies have so far tested commercial products, which only leads to hypotheses concerning the properties of particular monomers. However, some of their properties may be deduced from the chemical structure. Fig. 3 shows the chemical structure of several frequently used monomers in commercial adhesives. Next, we will discuss the main characteristics of some frequently used monomers.

2.1.1. Methacrylic acid (MA)

Because MA is a strong irritant and corrosive due to its strongly acidic nature, and because it can rapidly penetrate gloves and skin to cause allergic reactions, this monomer is hardly ever added to adhesives (Fig. 3). However, it is most probably present in varying amounts in the majority of adhesive resins, due to hydrolysis of the ester group in other monomers (Fig. 4). Hydrolysis of methacrylate monomers is generally an issue in SEAs, which standardly contain water and have a relatively low pH [50].

2.1.2. Methyl methacrylate (MMA)

Like MA, MMA is one of the oldest monomers and is very sporadically added to adhesives (Fig. 3). Again, due to its small molecular dimensions, this monomer is at high risk to elicit allergic reactions [51]. Use for cosmetic purposes has already been banned for this reason. Its function in adhesives is restricted to dissolving other monomers.

2.1.3. HEMA

HEMA is a small monomer that is in widespread use [52], not only in dentistry (Fig. 3). Its popularity in medical applications must be attributed to its relatively good biocompatibility [53], even though the uncured monomer is notorious for its high allergenic potential [54,55]. Uncured HEMA presents as a fluid that is well solvable in water, ethanol and/or acetone. Moreover, HEMA has been described to be able to evaporate from the adhesive solutions, though only in very small amounts [56].

Another important characteristic of HEMA is its hydrophilicity. Even though this monomer cannot be used as a demineralizing agent, its hydrophilicity makes it an excellent adhesion-promoting monomer [57–61]. By enhancing wetting of dentin, HEMA significantly improves bond strengths [62,63]. Nevertheless, both in uncured and cured state, HEMA will readily absorb water. Jacobsen and Söderholm hypothesized that HEMA-containing adhesives are more susceptible to water contamination, as the HEMA in the uncured adhesive may absorb water, which can lead to dilution of the monomers to the extent that polymerization is inhibited [64]. HEMA fixed in a polymer chain after polymerizing will still exhibit hydrophilic properties and will lead to water uptake with consequent swelling and discoloration [59]. Apart from the water uptake, which adversely influences the mechanical strength, high amounts of HEMA will result in flexible
polymers with inferior qualities [27]. PolyHEMA is basically a flexible porous polymer (‘gel’) [65,66]. As such, high concentrations of HEMA in an adhesive may have deteriorating effects on the mechanical properties of the resulting polymer. HEMA also lowers the vapor pressure of water, and probably also of alcohol. High amounts may therefore hinder good solvent evaporation from adhesive solutions [56]. Like all methacrylates, HEMA is vulnerable to hydrolysis, especially at basic pH, but also at acidic pH [67] (Fig. 4). HEMA is very frequently added to adhesives, not only to ensure good wetting, but also because of its solvent-like nature. This property improves the stability of solutions containing hydrophobic and hydrophilic components and will keep ingredients into solution [68].

2.1.4. 4-MET

4-MET is also frequently used, originally as an adhesion-promoting monomer [69], and later as a demineralizing monomer (Fig. 3) [70]. Moreover, 4-MET is known to improve wetting to metals, such as amalgam [71] or gold [72]. Its popularity is partially due to its easy synthesizing method and its being free of patent. 4-MET is easily available as its anhydride, 4-META, which is a crystalline powder. After addition of water to 4-META powder, an easy and swift hydrolysis reaction will take place to form 4-MET (Fig. 3). The two carboxylic groups attached to the aromatic group provide acidic and thus demineralizing properties, and also enhance wetting. The aromatic group, however, is hydrophobic and will moderate the acidity and the hydrophilicity of the carboxyl groups [73]. As a consequence, this monomer is well solvable in acetone, moderately solvable in ethanol, and difficultly solvable in water. Nevertheless, ethanol is not an appropriate solvent for this monomer as esterification of the carboxylic group for demineralization and adhesion promotion. A negligible amount of di-ethyl ester of 4-MET will also be formed.

2.1.5. 4-AETA

4-AETA differs from the structure of 4-META only by having an acrylate polymerizable group instead of a methacrylate group (Fig. 3). This group is regarded as an advantage for better polymerization [76]. No information could be found in literature as to differences in bonding effectiveness between 4-AETA and 4-META. Apart from facilitating resin penetration into dentin, the highly reactive acrylate group of 4-AETA is regarded as an advantage for better polymerization [76]. This functional monomer can be found in products of Shofu [77].

2.1.6. 10-MDP

10-MDP is a monomer that was originally synthesized by Kuraray (Osaka, Japan) and hence patented by them (Fig. 3). It is mainly used as an etching monomer, due to the dihydrogenphosphate group, which can dissociate in water to form two protons [50]. Structurally, the long carbonyl chain renders this monomer quite hydrophobic. As a consequence, ethanol and acetone are most suitable solvents for this monomer. Also, it is clear that 10-MDP will be relatively hydrolysis stable, as water will be kept at a distance. Yoshida et al. [7] showed that this monomer is capable of forming strong ionic bonds with calcium due to the low dissolution rate of the resulting Ca-salt in its own solution. In this study, 10-MDP was rated as the most promising monomer for chemical bonding to hydroxyapatite of enamel or dentin, as opposed to 4-MET and

![Fig. 5. Esterification of 4-MET when mixed with ethanol as solvent. One of the carboxylic groups may react in an esterification reaction with subsequent inactivation of the carboxylic group for demineralization and adhesion promotion. A negligible amount of di-ethyl ester of 4-MET will also be formed.](image-url)
2.1.8. Phenyl-P

Phenyl-P. The good in vitro and clinical outcome of Clearfil SE Bond from Kuraray [8,78,79], which is a 2-SEA that contains 10-MDP, may be partly attributed to the intense chemical adhesion with tooth tissue.

2.1.7. MAC-10

This monomer can be found in products by the Japanese manufacturer Tokuyama (Fig. 3). Information about this monomer in literature is very scarce. However, several properties can still be deducted from its chemical structure. Like 10-MDP, MAC-10 has a spacer group consisting of 10 carbon atoms. This for sure makes this monomer rather hydrophobic, which may reflect in limited dissolution in water. As the spacer group will not attract water, this monomer is probably also relatively hydrolytically stable.

2.1.8. Phenyl-P

Phenyl-P was used as one of the first acidic monomers in self-etching primers (Fig. 3) [26,80,81]. This monomer has also been described to promote diffusion of resin in demineralized dentin [82–84]. The monohydrogenphosphate group of this functional monomer can dissociate to form one proton. Phenyl-P has only very little chemical bonding capacity to hydroxyapatite [7]. This monomer is not frequently used anymore in contemporary adhesives (Table 1).

2.1.9. Di-HEMA-phosphate and HEMA-phosphate

HEMA-phosphate (also called MEP, 2-methacryloyloxyethyl dihydrogen phosphate), and most probably also di-HEMA-phosphate are hydrolytically instable (Fig. 3) [20]. In aqueous solutions, they will dissociate into HEMA and the strongly acidic phosphoric acid. Adhesive systems that contain these monomers may therefore be quite acidic. Prompt-L-Pop (3M ESPE) is a two-component one-step self-etch adhesive that contains such methacrylated phosphoric acid–HEMA esters [85]. It has been repeatedly reported to exhibit a low pH, which results in a profound demineralization of enamel and dentin [27]. The main disadvantage of hydrolytic degradation into HEMA and phosphoric acid, may be a dissimilar depth of penetration and demineralization. Incomplete infiltration of resin into the demineralized dentin is regarded as one of the drawbacks of E&R adhesives and ‘strong’ SEA, and may jeopardize longevity of adhesion [86,87]. Wang and Spencer [88] also reported a continued dentin demineralization effect of Prompt-L-Pop after 1 month storage in water. Apart from incomplete polymerization of the monomers as suggested, continued hydrolysis after curing, and release of phosphoric acid could account for the continuation of dentin demineralization.

2.1.10. Di-methacrylates

Bis-GMA, UDMA and TEGDMA are most frequently used cross-linkers in adhesive systems (Fig. 3). Other cross-linking monomers are also shown in Fig. 3. They directly provide mechanical strength to the adhesive system by forming densely cross-linked polymers [25]. When compared to the mono-methacrylate monomers in adhesives, they are usually characterized by hydrophobic behavior, which makes them only limitedly solvable in water. This feature will also prevent substantial water uptake after curing with attendant discoloration of the adhesive resin. Nevertheless, some water sorption is inevitable due to the polar ether-linkages and/or hydroxyl groups [18,89]. A ranking in amount of water sorption could be made: TEGDMA > Bis-GMA > UDMA [89]. Often, adhesive resins consist of mixtures of cross-linking monomers, and the relative amounts of Bis-GMA, TEGDMA and UDMA used will have a significant influence on the viscosity of the uncured adhesive resin [90] and on the mechanical properties of the cured resin [12,91].

Bis-GMA, also called ‘Bowen-resin’ after its inventor, is universally used, not only in adhesives but also in composites. The core of this monomer is identical to the one of Bisphenol A diglycidyl ether, an epoxy monomer. Uncured, Bis-GMA is highly viscous. Due to its high molecular weight, Bis-GMA provides lower polymerization shrinkage and rapid hardening, and the resulting polymer is characterized by superior mechanical qualities [18]. The two voluminous aromatic rings in the spacer also make this monomer quite rigid. This property has shown to have a negative effect on conversion rate, as the polymerizable methacrylate groups will have difficulty finding a mating methacrylate group. Admixture of other, lower-molecular-weight monomers is therefore required not to compromise polymerization [31]. Both monomethacrylates and other dimethacrylates such as UDMA, EGDMA or TEGDMA are used as ‘diluents’ [92,93].

TEGDMA is usually used in conjunction with Bis-GMA or UDMA. The higher flexibility of TEGDMA will compensate for the rigidity of Bis-GMA and admixture will result in resins with higher conversion rate [12]. In addition, this was also shown to result in increased tensile but reduced flexural strength of the resulting polymer [91].

Although a whole group of urethane dimethacrylates exist, UDMA (also called UEDMA) (Fig. 3) is most commonly used in adhesives. In spite of its comparable molecular weight to that of Bis-GMA, UDMA exhibits lower viscosity properties. In adhesives, UDMA is often used alone, or in combination with TEGDMA and/or Bis-GMA. Its main difference from the latter is its flexibility, as the ether bonds in UDMA allow easy rotation as compared to the two bulky aromatic rings in Bis-GMA [18].

Some controversy exists about the biocompatibility of these monomers. Apart from cytotoxicity, estrogenic activity has been assigned to Bis-GMA. Moreover, some studies indicated adverse effects of both Bis-GMA and TEGDMA on the fertility of both male and female mice [94–96]. It has been speculated that Bis-GMA may be metabolized, by combined hydrolytical and enzymatic degradation to form Bisphenol A, a compound with known estrogenic activity [18,97,98]. Release of Bisphenol A from Bis-GMA-containing resins is however
still a matter of controversy. Some authors have demonstrated its presence in saliva [99–101], while other researchers concluded that the amounts of released Bisphenol A are negligible [48,49,102]. Some manufacturers have addressed this issue by omitting Bis-GMA from their adhesive formulations.

2.1.11. (Meth)acrylamides

(Meth)acrylamides have an amide (–CO–NH– or –CO–N–) group instead of an ester group (–CO–O–R–) as in conventional acrylates and methacrylates (Fig. 2) [14]. Several amide monomers were investigated in experimental adhesives in the past [24,103–108]. The rationale for the use of amide monomers is their similarity to the amino acids of which collagen consist [107], which promotes the formation of hydrogen bonds between the carboxyl and amide groups of the monomer with the carboxyl groups of collagen [109–111]. Some experimental adhesives with amino-acid-like priming monomers achieved equal or better bond strengths than HEMA [104]. Recently, acrylamides have regained attention due to the better hydrolytic resistance of the amide as compared to the ester group (CO–O–R) of conventional (meth)acrylates [20–22]. The advent of self-etch adhesives, which standardly contain water and have an acidic pH, entails the problem of hydrolysis of monomers and subsequent reduced shelf life. AdheSE, a 2-SEA (Ivoclar-Vivadent) contains a bis-acrylamide in order to improve the shelf life of the adhesive. Many other (bis)acrylamides have been synthetized, but more research is needed concerning their features (solubility, polymerization reactivity, biocompatibility…) [22].

2.2. Initiator systems

It is generally accepted that adhesive systems should best be cured before the application of the composite, first to obtain an optimal degree of conversion and good mechanical strength of the adhesive layer [112], and second to prevent overly thinning of the adhesive resin layer by the application of the composite. The monomers in dental resins polymerize thanks to a radical polymerization reaction (Fig. 6) [113,114]. In order to set off this reaction, small amounts of initiator are required, which will be consumed during the polymerization reaction [14]. Initiators are generally molecules that possess atomic bonds with low dissociation energy that will form radicals under certain conditions [14]. Those radicals will set off the radical polymerization reaction. The amount of initiator was shown to be directly linked to the mechanical strength of the resin [115,116]. Nevertheless, the importance of the initiator is often overlooked [117].

Radicals can be produced by a variety of thermal, photochemical and redox methods [14]. In composite materials and their adhesives, redox as well as photo-activated initiators are used (Fig. 7). Photo-initiators absorb electromagnetic energy (photo-curing), while redox initiators need admixture of another component (chemical curing or self-curing). The choice between photo-initiation and self-curing depends on the purpose of the adhesive system. The main advantage of polymerization started by irradiation is the easy control on the onset of the reaction. However, whenever radiation is hampered to reach the adhesive, self-curing systems are the better choice. Generally, adhesive systems devised to bond composite fillings utilize photo-initiators, whereas resin-based cements usually rely on chemical initiation. When both photo-initiators and chemically curing initiators are added, the adhesive resin is said to be ‘dual-curing’. The aim of this double setting mechanism in dual-cure resins is mainly to boost the polymerization and consequently to achieve a higher degree of conversion, especially at areas remote or hidden from the light source.

The amount of initiator added to adhesive systems depends on the type of initiator and on the adhesive system, but is usually very small, in the range of 0.1–1 wt%. Optimal initiator/co-initiator concentrations in adhesives depend on many factors, such as solubility of these compounds in the monomer—solvent mixture, the absorption characteristics and compatibility with the used light-curing unit, photo-reactivity (effectiveness to produce radicals), color, and biocompatibility. In contrast to composite filling materials, the polarity of the initiator/co-initiator system must be taken into account when added to hydrophilic adhesive systems, in order to obtain homogenous polymerization [118,119].

The biocompatibility of adhesives is declined by the addition of initiators. They have mainly been associated with cytotoxicity, related to their ability to generate free radicals [120–122].

2.2.1. Photo-initiators

Many compounds can dissociate into radicals upon absorption of light energy. Although they can produce free radicals by several mechanisms, they usually contain a keton (C = O), the electrons of which can be promoted into a higher orbital by the absorption of the required wavelength (excitation) [123]. Subsequently, they can undergo either decomposition to yield free radicals (type I or photo-fragmentation photo-initiator, like benzoin esters, benzophenone, acylphosphine oxides, PPD), or a bimolecular reaction where the excited state of the photo-initiator interacts with a second molecule (a co-initiator) to produce free radicals (type II or electron-transfer photo-initiator like camphorquinone (CQ), PPD) [14]. In the latter reaction, a co-initiator is added to the photo-initiator. Aliphatic and aromatic amine compounds have proven to be efficient hydrogen donating co-initiators. Several problems, however, have been associated with amine co-initiators in adhesive systems. As amines are nucleophilic, an acid–base reaction between the amine co-initiator and the acidic monomers cannot be excluded [22,124]. This reaction will lead to protonization of a moiety of the amine, according to the equilibrium of the
acid–base reaction, and thus, to a decrease of the available amine that will form amine radicals. The amine concentration in adhesives therefore needs to be exactly adjusted to the concentration of acidic monomers [22]. Using a second co-initiator that will not be deactivated is always recommendable in acidic adhesives [23]. Finger et al. [125] showed that addition of an anionic resin to acidic adhesive resins may help to overcome incompatibility problems.

Good dosing of the added amount of amines is also indispensable as the by-product of tertiary amines by degradation are notorious for inducing discoloration with time, especially when added in high concentrations [126,127]. Moreover, amines used as co-initiator have been described to have limited biocompatibility and have been shown to be both toxic and mutagenic [53,128]. A wide variety of amines can be employed, some of which are also

Fig. 6. (Meth)acrylates and (meth)acrylamides in adhesives polymerize due to a radical polymerization reaction. At the top of the figure, the radicalization reaction of two main initiators in dental adhesives is shown. Camphorquinone is a typical photo-initiator, while benzoylperoxide is a thermal initiator that also can be used in a redox reaction. Both initiators function with a co-initiator, which usually is a tertiary amine compound. At the bottom, the polymerization reaction of methacrylates is shown. This reaction can be subdivided in an initiation, propagation and deactivation reaction. Termination of the polymerization reaction refers to a bimolecular reaction by combination or disproportionation that leads to the deactivation of the propagating radical chain ends. Combination refers to the reaction of two radical chain ends and disproportioning involves hydrogen transfer and formation of two dead polymer chains (one saturated and one unsaturated) [113,114].
methacrylates that can be polymerized, which is assumed to reduce toxicity [112,128].
One of the main characteristics of photo-initiators is their peak absorption wavelength and their absorption spectrum. Commonly, photo-initiators absorbing in the visible light spectrum are preferred. The absorption of photo-initiators should correlate with the emission profiles of dental curing units [129]. Moreover, the maximum absorption wavelength varies depending on the solvent, in which the photo-initiator is dissolved. Generally, the maximum absorption wavelength shifts to lower wavelengths with increasing polarity of the solvent [116,130]. For adhesive systems that contain high amounts of solvent, like 1-SEAs, these absorbance shifts may influence polymerization when a narrow spectral emission light source (for example LED) is employed [130]. LED light-curing units are becoming increasingly popular, and it can be foreseen that they will eventually replace halogen light-curing units. LED units however have a narrow emission spectrum as opposed to halogen units, and their emission is generally optimized for the use of CQ in dental resins. The increased use of LED has urged many manufacturers that used to add alternative photo-initiators with different absorption spectra, to choose again for CQ.

2.3. Camphorquinone/co-initiator system

Among the most popular photo-initiators in adhesives (and also composites) is CQ combined with a co-initiator [131] (Figs. 6 and 7). After excitation by blue light, an excited complex will be formed yielding radicals by ‘hydrogen abstraction’ (Fig. 6). Amines are efficient hydrogen donors, and are extensively used. The effectiveness of several different co-initiators in conjunction with CQ has been tested [119,132]. CQ is an excellent photo-initiator that absorbs over a wide spectrum of wavelengths from 360–510 nm, with peak absorbance around 468 nm (blue light). When dissolved in water, the absorption peak shifts to lower wavelength of 457 nm, while dissolution in a less polar environment such as TEGDMA results in a bathochrome shift of the absorption spectrum with a peak at 474 nm [130]. Its broad absorption spectrum is an advantage. At room temperature, CQ is a crystalline powder, and this molecule is only limitedly solvable in water. One of the main disadvantages of CQ is its inherently yellowish-brown color. Even though this initiator is usually used in minute amounts (0.03–01%), it influences the color of the adhesive resin significantly [127]. Notwithstanding that the yellow color partially fades after curing, the remaining yellow color may possibly cause problems in color matching, especially nowadays with the trend of bleaching. This issue limits the amount of camphorquinone used in both composites and adhesive resin. This initiator has also been shown to be cytotoxic [122,133].

2.4. 1-phenyl-1,2 propanedione (PPD)

The diketone PPD (Fig. 7) has recently been introduced as a photo-initiator for dental resins [134], and yields radicals both by cleavage and by proton transfer from an amine co-initiator [123]. Compared to CQ, PPD absorbs mainly over a spectrum with higher energy, but its absorption profile extents into the visible range. Neumann et al. [129] found that PPD was activated similarly by both LED and halogen light-curing units. Its peak absorbance is in the vicinity of 400 nm [116]. Unlike CQ, PPD is a slightly yellow viscous fluid at room temperature. This physical state allows PPD good compatibility with resin, where it serves as a diluent as opposed to CQ. Its less intense yellow color is also an advantage over CQ [123]. Sun and Chae showed that PPD yields higher mechanical strengths, and PPD has comparable or better polymerization efficiency than CQ [116,123,135]. When used in combination with CQ, PPD acts synergistically [123].

2.5. Acylphosphine oxides

Acylphosphines represent a wide group of photofragmentation photo-initiators for free-radical polymerization.
processes (Fig. 7). They have a strong absorption near the UV light, also extending into the visible part of the spectrum [129]. Examples in dental resins would be (2,4,6-trimethylbenzoyl)diphenylphosphine oxide or TPO (Lucirin TPO, BASF), a monoacrylphosphine (Fig. 7) and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide or Irgacure 819 (Ciba-Geigy). Their neutral color, as opposed to camphorquinone, is an important advantage. The popularity of TPO, however, is diminishing due to the increased use of LED curing units, which are not appropriate for curing TPO-containing resins. Neumann et al. [129], however, found that Irgacure is best light cured by a high-power LED device. Due to the three-phenyl groups, TPO and also Irgacure are rather hydrophobic molecules that are difficultly dissolvable in water [136]. These photo-initiators are therefore less suitable for water-containing adhesive systems, like 1-SEAs. Moreover, the stability of phosphine oxides is not guaranteed in the presence of water and ethanol [22].

2.5.1. Chemical initiators

The use of chemical initiators is usually restricted to cements and resin that cannot rely (solely) on light curing for polymerization. Adhesives that are chemically curing generally need the admixture of the initiator with the co-initiator, after which the setting reaction will start. Inherently, they consist of two separate bottles, the content of which need to be mixed before application onto the tooth surface. The most common initiator in self-curing resins would be benzylperoxide (BPO) in conjunction with a tertiary amine [23,120] (Figs. 6 and 7). BPO will react with the tertiary amine as a co-initiator, yielding radicals (Fig. 6). It is a colorless, crystalline solid, that is very limitedly soluble in water, but soluble in ethanol and acetone. Like all organic peroxides, BPO undergoes slow photolysis when exposed to light, and self-curing adhesives should therefore always be stored in darkness. Elevated temperatures will also favor the formation of radicals [14].

Storage in the refrigerator is thus recommended. When dissolved in water, BPO undergoes rapid hydrolysis, depending on the pH (better shelf life at acidic pHs). As a consequence, BPO should not be used in water-containing adhesives, unless it is stored in a different bottle. The same issues that arise from the use of amines with photoinitiators (see above), such as neutralization in acidic solutions, discoloration and toxicity, occur also in self-curing systems with amines.

Tri-n-butyl borane (TBB) (Fig. 7) is another initiator compound [137], described many times in research literature [138]. Its commercial use is, however, restricted to a couple of adhesives used for cementation (C&B Super-Bond Sun Medical and C&B Metabond, Parkell). TBB is a very reactive molecule-producing radicals by an autoxidation process (reaction with oxygen), which gives it its excellent polymerization capacity (Fig. 7). No co-initiator is required. However, this compound is also very instable in water, air (self-ignating) and acid, which severely restricts its use. Separate recipients are indispensable. In C&B Super-Bond and in C&B Metabond, TBB is delivered in separate metal syringes.

2.6. Inhibitors

Inhibitors added to dental resins are actually antioxidants that are able to scavenge free radicals originating from prematurely reacted initiators. Especially in extreme storage conditions, such as high temperatures (for example during transport and shipping), some initiator molecules may decompose or react spontaneously to form radicals. Inhibitors and retarders will then prevent spontaneous initiation and propagation of the free-radical polymerization reaction by readily quenching these radicals [14]. As such, inhibitors promote shelf life. The required inhibitor concentration depends on the inherent instability of the monomers in the adhesive (acrylate versus methacrylate). The effect of inhibitors on the actual polymerization is negligible since only minute amounts are used. When the polymerization reaction is set off by either light curing or admixture of two components, a much higher amount of radicals will be formed, outweighing the amount of inhibitor. The firstly formed radicals will still be neutralized by the small amount of inhibitor, after which the polymerization reaction will start off, initiated by the surplus of radicals available [139]. Great amounts of inhibitor, however, can induce a decrease of cure rate. A good balance must be struck between shelf life and cure speed, and between the concentration of initiator and inhibitor.

The most frequently used inhibitors in adhesives are butylated hydroxytoluene, also butylhydroxytoluene (BHT) and monomethyl ether hydroquinone (MEHQ) (Fig. 8). Whereas BHT is most often used in composites and hydrophobic adhesive resins, MEHQ is preferred for more hydrophilic resins. Due to its hydrophobic nature, BHT is frequently added as a food preservative for fats (E321). Both inhibitors have been shown to elute from resins and so far, these compounds deserve careful evaluation for biocompatibility [29,140].

2.7. Solvent

The addition of solvents to resins is indispensable to the composition of adhesives that need to bond to dentin. The wet nature of dentine only allows good wetting when a hydrophilic bonding is applied [26]. By adding hydrophilic monomers on the one hand, and a solvent on the other hand, the wetting behavior of the adhesive is drastically improved [141]. The low viscosity of primers and/or adhesive resins is partly due to the dissolution of the monomers in a solvent and will improve its diffusion ability in the micro-retentive tooth surface. In E&Rs, the main function of the solvent, present within the primer of 3-E&Rs, and within the combined primer-adhesive resin (‘one-bottle systems’) in 2-E&Rs (Fig. 1), is to promote...
good penetration of the monomers in the collagen network of the demineralized dentin [142]. In case of bonding to air-dried dentin, the solvent should also be capable of re-expanding the collapsed network [64,143]. In SEAs, the use of water as a solvent is indispensable to ensure ionization of the acidic monomers [66,144].

Solvents are substances that are capable of dissolving or dispersing one or more other substances [145]. When a solvent dissolves a solid or a liquid, the molecules (or ions) become separated from each other and the spaces in between become occupied by solvent molecules. The energy required to break the bonds between solute molecules is supplied by the formation of bonds between the solute particles and the solvent molecules; the old intermolecular forces are replaced by new ones. The solubility characteristics of molecules are determined chiefly by their polarity. Non-polar or weakly polar compounds dissolve in non-polar or weakly polar solvents; highly polar compounds dissolve in highly polar solvents (‘like dissolves like’). The polarity of solvents is determined by both the dipole moment and the dielectric constant [145]. Chemists have classified solvents into three categories according to their polarity: polar protic, dipolar aprotic and apolar solvents. Polar protic solvents consist of a hydroxyl-group that can form strong hydrogen bonds. Examples are water and ethanol. Polar aprotic solvents do not have the required hydroxyl-group to form hydrogen bonds, but do have a large dipole moment. They usually also contain a keton group. Typical example is acetone. Apolar solvents have both a low dielectric constant and dipole moment. The polarity of a solvent is also important to predict the shelf life of adhesives, as apolar solvents will more easily pass through traditional polyethylene packaging.

In adhesives, water, ethanol and acetone are the most commonly used solvents (Table 3). Other polyvalent alcohol solvents have been evaluated, but are not used commercially [146]. The use of these organic solvents in adhesives must be explained by their inexpensiveness, their wide availability, and their good biocompatibility. Most other typical solvents are toxic. MMA and HEMA, both small monomer compounds have also been described as diluents for other monomers and can therefore also be called solvents. Moreover, the hydroxyl-group of HEMA also provides in hydrogen bonds [147]. However, the H-bonding capacity of HEMA is limited. DENTSPLY added tert-butanol to a recent 2-E&R, because of its similar vapor pressure as ethanol, but better stability towards chemical reaction with monomers.

Most important characteristics of a solvent are its dipole moment, dielectric constant, boiling point, vapor pressure and H-bonding capacity (Table 3). The vapor pressure of a solvent is important to ensure good evaporation of the solvent after application of the adhesive onto tooth tissue [148,149]. Air-drying after application also facilitates the removal of remaining solvent from the adhesive [150]. In addition, air-drying will decrease the thickness of the adhesive layer, which has been shown to promote further solvent removal [151]. Complete evaporation is however difficult to achieve and is hampered by the short clinical air-blowing time [42,149]. Remaining solvent in the adhesive may jeopardize polymerization due to dilution of the monomers and may result in voids and hence permeability of the adhesive layer [64,152,153]. Instructions for air-blowing solvent-free adhesive resins of course do not envisage solvent evaporation, but intend to render the adhesive layer uniform and even.

The H-bonding capacity of a solvent has been shown to be important to re-expand the shrunken demineralized collagen network after dehydration [147,154]. Solvents that have higher affinity to form H-bonds, will be able to break stabilizing H-bonds and other forces that keep the collagen in shrunken state.

2.7.1. Water

Water is a strongly polar solvent with a high dielectric constant, capable of dissolving ionic lattices and polar compounds. Its dissolving capacity is greatly determined by

<table>
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<th>Solvent</th>
<th>Dipole moment in gaseous state in Debye at 25 °C</th>
<th>Dielectric constant at 293 K (20 °C)</th>
<th>Boiling temperature (°C)</th>
<th>Vapor pressure in mmHg at 25 °C</th>
<th>H-bonding capacity</th>
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</thead>
<tbody>
<tr>
<td>Water (H₂O)</td>
<td>1.85</td>
<td>80</td>
<td>100.0</td>
<td>23.8</td>
<td>+++</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.69</td>
<td>24.3</td>
<td>78.5</td>
<td>54.1</td>
<td>+</td>
</tr>
<tr>
<td>CH₃-Et-OH</td>
<td>2.88</td>
<td>20.7</td>
<td>56.2</td>
<td>200</td>
<td>–</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-Butanol</td>
<td></td>
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![Chemical structure of the two most frequently used inhibitors in adhesive systems. Abbreviations: BHT: butylated hydroxytoluene; MEHQ: monomethyl ether hydroquinone.](image-url)
its capability of forming strong hydrogen bonds. However, water is a poor solvent for organic compounds (such as monomers), which are usually rather hydrophobic. This difficulty can be overcome by addition of a secondary solvent, such as ethanol or acetone.

As mentioned before, water is an indispensable compound of SEAs, in order to ionize the acidic monomers. However, the higher the concentration of co-solvents added, the fewer protons there will be formed [145]. In E&Rs, water is capable of re-expanding the collapsed and shrunken collagen network [155,156]. Thanks to its high dielectric constant, only water is capable of breaking the hydrogen bonds between the collagen fibers [63,156–158].

Yet, the high boiling temperature and low vapor pressure of water imply that this solvent is difficult to remove from adhesive solutions after application on the tooth. In addition, the equilibrium of water between fluid and gaseous state is also in favor of the fluid state in the already damp oral environment, which will decrease the rate of evaporation even more [56]. Moreover, Pashley et al. [56] showed that monomers, such as HEMA, decrease the vapor pressure of water even more, which may interfere with the removal of the last amounts of water. Tay et al. [159] showed that excess water in the adhesive resin compromises the bond strength of adhesives due to entrapment of water blisters (‘overwet phenomenon’).

2.7.2. Ethanol

Like water, ethanol is a polar solvent that will form hydrogen bonds with its solutes. However, due to its much lower dielectric constant, ethanol is also a more appropriate solvent for less polar solutes. Its higher vapor pressure as compared to water allows better evaporation by air-drying. Usually ethanol is used in conjunction with water as co-solvent. Moreover, water–alcohol mixtures are known to be ‘azeotropic’ [22,145]. This implies the formation of hydrogen bonds between water and ethanol molecules, resulting in a better evaporation of these water–ethanol aggregates than pure water. Self-evidently, this results in more water removal from the adhesive and in increased surface dehydration. Maciel et al. [157] showed that ethanol has a stiffening effect on demineralized collagen. This feature may also explain why ethanol can maintain wide interfibrillar spaces after evaporation of the solvent [156]. Ethanol is not an appropriate solvent for monomers with carboxylic acid moieties. Depending on the reactivity, carboxylic acids esterify (esterification reaction) with alcohols (Fig. 5), which may lead to inactivation of the acidic function of the monomer.

2.7.3. Acetone

Acetone’s high dipole moment in combination with its relatively low dielectric constant allows mutually dissolving polar and apolar compounds. For this reason, acetone is a good choice of solvent in adhesives that combine hydrophobic and hydrophilic components. Its high vapor pressure, which is about four times as high as that of ethanol, is a main advantage. However, its high volatility may also lead to reduce shelf life of acetone-containing adhesives, by rapid evaporation of the solvent. Acetone is frequently used as a solvent alone, but in SEAs it comes as co-solvent with water. Similar to ethanol, acetone and water make an azeotrope. Although the formation of hydrogen bonds is much lower with ketons (C═O) than with alcohols (–OH), acetone has a very good water-removing capacity, because of its high dipole moment and excellent evaporation capacities [148]. This is often referred to as the ‘water-chasing’ capacity of acetone [64]. Wet-bonding E&R systems usually contain acetone to facilitate water removal [154,160]. These systems should be applied on demineralized dentin that is kept in a wet state in order to prevent collagen collapse, a technique coined ‘wet-bonding technique’. The acetone of adhesives that follow this strategy must ensure enhanced evaporation of water left in dentin. Considering the low H-bonding capacity of acetone, it is not able to re-expand shrunken demineralized collagen [154].

2.8. Filler

Whereas composite resins by definition always contain filler particles, this is not always the case for adhesive resins. Adhesives containing fillers are said to be ‘filled’, in contrast to ‘unfilled’ adhesives (Fig. 9). Adhesive systems for bonding direct restorations to tooth tissue traditionally did not contain filler particles [161].

Fillers can be added to adhesives for several reasons. The adhesive resin layer, situated between the composite filling and the tooth, is considered to be a weak link due to its low tensile strength and low elastic modulus [32]. By analogy with composites [162], several authors have suggested that the addition of fillers may fortify the adhesive layer [163–166]. However, the relevance of the strengthening effect of the filler in adhesive resins is controversial, especially because only small concentrations of fillers are added to adhesive resins [167]. Secondly, manufacturers often add filler particles to modify the viscosity of adhesives. Moreover, their thickening effect prevents overly thinning of the adhesive layer [85]. Too thin an adhesive layer may suffer from incomplete resin polymerization due to oxygen inhibition. It was shown that filled adhesives yield thicker adhesive layers after air thinning [161,168]. Moreover, thicker adhesive layers may also provide good relief of contraction stresses produced by the restorative resin composite, thanks to their inherently higher elasticity [169,170]. Depending on their chemical composition, fillers can also provide in fluoride release and radio-opacity, which may prove important when the adhesive is applied in relatively thick layers and differential diagnosis with recurrent caries is necessary.

With regard to the filler content and size, adhesive resins differ in two aspects from composite filling materials. First, only low amounts of filler are appropriate in filled adhesives, so as not to compromise the wetting of the
bonding substrate due to high viscosity. Moreover, adhesive systems that consist of separate resins (3-E&R and 2-SEAs) are usually more loaded than adhesives that combine the hydrophobic resins with the priming and/or acidic monomers (2-E&R and 1-SEAs) [168] (Fig. 1). Some adhesive resins tend to produce a thicker adhesive layer, even after strong air-blowing the adhesive before light-curing (as per manufacturer’s instructions). (c) TEM of Clearfil Protect Bond (Kuraray), immersed in silver nitrate to disclose nanoleakage. Apart from silica filler in the adhesive layer, several distinct oblong filler particles can be seen. These filler particles are most probably the polysiloxane-encapsulated sodium fluoride particles. (d) TEM of Optibond FL (Kerr), a 3-E&R filled with a mixture of fumed silica, disodium hexafluorosilicate and barium aluminum borosilicate glass. The latter renders the rather thick adhesive layer (50 μm) of this adhesive radio-opaque. However, adhesive systems are generally not filled to a level, which will yield clinically effective radio-opacity. Notice that these borosilicate glass particles are also much larger than silica.

Fig. 9. Transmission electron photomicrographs showing the adhesive layer of several adhesives bonded to dentin. (a) TEM of iBond (Heraeus-Kulzer), an unfilled 1-SEA. No filler particles can be found in the adhesive layer. (b) TEM of G-Bond (GC), a 1-SEA filled with nano-sized silica particles. Filled adhesive resins tend to produce a thicker adhesive layer, even after strong air-blowing the adhesive before light-curing (as per manufacturer’s instructions). (c) TEM of Clearfil Protect Bond (Kuraray), immersed in silver nitrate to disclose nanoleakage. Apart from silica filler in the adhesive layer, several distinct oblong filler particles can be seen. These filler particles are most probably the polysiloxane-encapsulated sodium fluoride particles. (d) TEM of Optibond FL (Kerr), a 3-E&R filled with a mixture of fumed silica, disodium hexafluorosilicate and barium aluminum borosilicate glass. The latter renders the rather thick adhesive layer (50 μm) of this adhesive radio-opaque. However, adhesive systems are generally not filled to a level, which will yield clinically effective radio-opacity. Notice that these borosilicate glass particles are also much larger than silica.

The surface chemistry of the filler particles determines their hydrophilic behavior. In contrast to composite filling materials and low-viscosity adhesive resins, hydrophilic adhesives like 2-E&R and especially 1-SEAs may be better off with hydrophilic filler particles. Both hydrophilic and hydrophobic silica can be purchased from manufacturers (Degussa, Germany). The silanol (-Si-OH) groups of untreated silica account for the hydrophilic behavior of the filler particles. Hydrophobized silica has dimethylsilyl (-Si-(CH₃)₂-) and trimethylsilyl (-Si-(CH₃)₃) groups at the surface. Most adhesive systems contain hydrophobic fillers [166]. Kim et al. [166] tested different concentrations of hydrophilic nanofiller in a 2-E&R system. In spite of the hydrophilic composition of the experimental adhesives in this study and the wet-bonding protocol, concentrations of 3 wt% filler already tended to cluster, hence decreasing the bond strength. Some manufacturers use functionalized nanofillers to prevent them from clustering (DENTSPLY).

Generally, fillers in adhesive resins are silanized to allow for chemical bonding between the filler and the resin matrix. Silane coupling protects the adhesive resin against premature degradation and improves the stress transmission between the resin matrix and filler particles [174].
2.9. Specific ingredients

Manufacturers sometimes add specific ingredients. The adhesives of 3M ESPE (Adper Prompt, Single Bond, Scotchbond Multipurpose) often contain a specific poly-alkenoic copolymer (Fig. 10). The rationale for the use of this polymer is to provide better moisture stability [86,175]. However, any positive effect of this compound on the bond strength so far remains unclear. Moreover, several authors have demonstrated that this monomer does not dissolve in the adhesive's solution, leading to a separate phase producing many globules within the polymer of the adhesive layer [175].

Another particular ingredient would be glutaraldehyde (Fig. 11). This compound is frequently used as fixator or disinfectant in several medical fields. In dentistry, it was introduced as a desensitizing agent for treating hypersensitive roots. Its desensitizing effect results from denaturation of collagen in dentin [176,177] and the occlusion of dentinal tubules [178]. The rationale for its use in dental adhesives is prevention of post-operative pain [179] and stabilization of the collagen fibers in the hybrid layer to improve durability [180]. The Gluma bonding systems by Heraeus-Kulzer (before Bayer) were the first adhesives that contained glutaraldehyde [179,181]. In response, several other manufacturers also added glutaraldehyde to their adhesive formulation (Syntac, Vivadent; ProBond, DENTSPLY Caulk). Generally, no more than 5% is added [177]. Additionally, glutaraldehyde has a strong antibacterial activity [181–183]. In spite of some promising effects of pre-treating etched dentin with glutaraldehyde [180], no actual beneficial effect of the use of this compound in bonding systems as compared to control adhesives has so far been proven [184–186]. Moreover, some concern has risen regarding the biocompatibility of glutaraldehyde [187], which is known for its toxic [188], allergic [189] and even mutagenic effects [190,191]. Apart from direct incidental contact with mucous tissues, inhalation of glutaraldehyde evaporated from the adhesive should be considered as a source of irritation and allergic asthma both for dentist and patient. Considering the hydrophilicity of glutaraldehyde (Fig. 11), stability problems in adhesives cannot be excluded.

Currently, inclusion of antibacterial adjuncts into the adhesive's formulation has become popular. The main aim of these antibacterial ingredients is preventing recurrent caries underneath composite fillings. Furthermore, they are also recommended when the clinical situation prevents complete caries removal. Examples of such antibacterial compounds are the MDPB monomer (described above), fluoride (see also fillers), and parabens (Adper Prompt-L-Pop, 3M ESPE) (Fig. 11). Apart from fluoride-releasing glass fillers, some manufactures also add simple fluorine compounds to their adhesives. Prime&Bond NT (DENTSPLY) contains cetylamine hydrofluoride (Hetaflur, C16H35NHF), also used as fluoride adjunct in toothpastes. In contrast to antibacterial monomers, which co-polymerize with the adhesive resin matrix, separate antibacterial agents will be left detached from the polymer matrix, and will leach out of the adhesive resin. Unfortunately, no clinical trials exist that could determine a clinical positive effect of adding antibacterial components to adhesives. Apart from persisting antibacterial effects, it is clear that these compounds could also pose biocompatibility problems.

Some manufacturers add dyes to self-etch adhesives (One-up Bond F, Tokuyama Japan; Tyrian SPE, Bisco, USA). The use of dyes facilitates homogeneous admixture of two components and better visual control of homogeneous spreading of the adhesive across the whole tooth surface [22]. After light curing, the bonding returns colorless. Tyrian SPE contains thymol blue, a dye that is actually an acid–base indicator (Fig. 11). Thymol blue is a weak acid that is yellow when undissociated. Upon ionization, this compound turns to a red color.

Some adhesives contain acids that are not monomers. Maleic acid is added to Syntac (Ivoclar-Vivadent) in order to render the primer acidic (Fig. 11). Similarly, silicic acid can be found in Absolute (DENTSPLY Sankin).

Fig. 10. Transmission electron photomicrograph of Adper Scotchbond XT1 (Scotchbond 1 XT) on dentin. TEM-section stained with uranyl acetate and lead citrate. Notice how the poly-alkenoic co-polymer forms a different phase in the adhesive layer, resulting in multiple globules with varying size.

Fig. 11. Manufacturers sometimes add specific ingredients. The chemical structure of some of these ingredients is shown in this figure.
3. Conclusion

Dental adhesives are intricate mixtures of ingredients. Profound knowledge of these ingredients is one key to better understanding the behavior of adhesives in studies and in clinic. Good understanding also provides better insights in the correct clinical use of adhesives. Each ingredient has to some extent a specific effect on the bond strength, bonding efficiency, bonding durability, shelf life and biocompatibility of the adhesive system. In addition, ingredients may affect each other in a complicated interplay of factors. Unbalanced mixtures of ingredients may lead to reduced bonding effectiveness, durability, shelf life and to phase-separation reactions, while a well thought-out formulation will be the key to long-term clinical success.

More research is warranted as to the biocompatibility of dental adhesives, as many ingredients exhibit cytotoxic properties, and some are even suspected to interfere hormonally. Moreover, systemic effects can so far not be excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded. For these reasons, pulp capping by directly applying the adhesive onto the exposed vital pulp seems excluded.

All in all, the chemical composition of contemporary adhesives determines their clinical success. Improving their clinical behavior can be achieved by two different means. The first way entails adjusting the proportional amount of ingredients in adhesives. Changing the number of bottles and adding or omitting application steps also boils down to changing the ‘cocktail formulation’ of adhesives. The second avenue to pursue is to design new components. In particular, monomers may be tailored to provide specific qualities concerning polymerization, wetting and chemical bonding. It is clear that the latter is a time-consuming and expensive method, which explains why only few companies choose to go this way. However, as the first method has already been extensively exploited, the development of new ingredients and custom-made monomers seems most promising for further significant improvement of adhesives.

Acknowledgments

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