SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
CONSULTA DE DOCUMENTOS

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RAD: 12-56629- -6 **FECHA:** 2013-07-25 18:11:58
DEP: 2020 DIRECCION DE NUEVAS CREACIONES **EVE:** 378 FASE NACIONAL INCLUIDO CAPITULO I
TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II **FOLIOS:** 5
ACT: 519 PRESENTACION

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
DILIA MARIA RODRIGUEZ D ALEMAN

Asunto:		
	Radicación:	12-56629- -6
	Trámite:	11
	Evento:	378
	Actuación:	519
	Oficio:	13514
	Folios:	5

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/US2010/047171				
Fecha de Presentación Internacional	30/08/2010				

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

:

Descripción:	Rad. N° 12-056629-00000-0000	04/Abril/2012
Reivindicaciones:	Rad. N° 12-056629-00004-0000	15/Marzo/2013
Prioridades:	US 12/573,633	05/Octubre/2009

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada.

Se aceptan para estudio todas las 41 reivindicaciones presentadas (Fls. 4 a 13 del Rad. N° 12-056629-00004-0000) porque las tasas pagadas cubren en su totalidad lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única.

Título de la solicitud: "Capa de color removible de protección para recubrimientos de uñas artificiales y métodos para ello" (Fl. 1).

El problema planteado en esta solicitud consiste en la necesidad de suministrar un recubrimiento para uñas de rápida curación y aplicación.

Para resolver este problema técnico, la solicitud en estudio proporciona una composición a base de esteres de celulosa y metacritalos etilénicamente insaturados para realizar polimerización tomando un fotoiniciador como iniciador de la reacción.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP) C08F 251/02.

4. Reivindicaciones relativas a un uso o a un segundo uso (Art 14 y 21 D 486)

El uso como recubrimiento para uñas de la reivindicación 41 no es patentable, de acuerdo con el Art 14.

5. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Las reivindicaciones 1 a 6, 9, 12 a 14, 18 a 22 y 24 a 38 no son claras porque las expresiones *"al menos" y "alrededor de"* son imprecisas, por lo cual no permiten distinguir la invención del estado de la técnica. Se sugiere sustituirlas por términos precisos o un rango concreto.

Las reivindicaciones 1 y 38 no son claras porque las expresiones "*con la exposición a un acelerador de la polimerización, dicha composición polimerizable cura a una rejilla de material temoendurecible acrílico que tiene huecos definidos en ella*" *y* "*una porción de los huecos contiene el al menos un polímero soluble en un disolvente no reactivo*" son resultados a alcanzar, lo que no está permitido, no define al producto y/o método porque la invención no queda definida por el resultado a alcanzar, puesto que la reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado. Se sugiere remplazarla por las características esenciales estructurales que contribuyen a la obtención de ese efecto.

La reivindicaciones 1, 15, 18, 21y 34 no son concisas porque las definiciones de monómero polimerizable por adición, polímero soluble, disolvente no reactivo, solvente no reactivo, met(acrilato) promotor de la adherencia, colorante, agente de reología y fotoiniciador, son géneros funcionales, se sugiere restringir la solicitud a una razonable generalización del tipo de compuestos que han sido sintetizados ó probados, es decir, que se encuentran debidamente sustentados.

La reivindicación 39 no es clara porque la expresión "*forma por curado una composición polimerizable*" no está justificada en la descripción, pues se indicaría que por un proceso de polimerización se produciría una composición. Se sugiere realizar la corrección necesaria.

La reivindicación 41 no es clara porque indica el uso que puede darse a la composición reivindicada, el cual no es una característica técnica que defina a la invención. Se sugiere hacer la aclaración respectiva.

La reivindicación 23 no es clara porque hace referencia a un producto, pero presenta características técnicas de un método al indicar que la sílice se modifica por polidimetilsiloxano. Al respecto no debe olvidarse que las reivindicaciones de producto y de procedimiento son diferentes y, por ello, deben redactarse de manera independiente en el pliego reivindicatorio. Sobre las mismas, el Tribunal Andino de Justica ha dicho lo siguiente:

> "El objeto de la invención de producto está constituido por un cuerpo cierto destinado a llenar una necesidad industrial que el estado de la técnica aún no ha satisfecho. En cambio, el objeto de la invención de procedimiento se encuentra conformado por "una serie o sucesión de operaciones que inciden sobre una materia (solida, liquida o gaseosa) que se encamina a la obtención de una cosa o un resultado"[1].

6. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad invocada, es decir, el 05 de octubre de 2009.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud.

Item	Documento	Título	Fecha de Publicación
D1	US 5985951	"UV-curable nail coating formulations containing cellulose esters with ethylenically unsaturated pendant groups"	16/Noviembre/1999
D2	US 5785958	"Non-yellowing rapid drying nail polish top-coat compositions"	28/Julio/1998

El documento D1[2] divulga una composición para recubrimiento de uñas a base de esteres de celulosa (Col. 1, líneas 13 a 21).

El documento D2[3] divulga una composición para recubrimiento de uñas a base de acetato butirato de celulosa y metacrilatos (Col. 2, líneas 47 a 61).

7. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 1 consiste en "*Una composición polimerizable que comprende: (i) al menos un monómero etilénicamente insaturado, polimerizable por adición; (ii) al menos un polímero…*" (Ver Fl. 4 del Rad. N° 12-056629-00004-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características **esenciales**	**D1**	**D2**
Composición polimerizable que comprende:	Composición polimerizable (Col. 1, líneas 13 a 21).	Composición polimerizable (Col. 2, líneas 47 a 61).

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[1] Otero Lastres, José Manuel. Ob. Cit. Proceso 129aIPa2007.

[2] http://worldwide.espacenet.com/publicationDetails/biblio?DB=worldwide.espacenet.com&II=0&ND=3&adjacent=true&locale=en_EP&FT=D&date=19991116&CC=US&NR=5985951A&KC=A

[3] http://worldwide.espacenet.com/publicationDetails/biblio?DB=worldwide.espacenet.com&II=0&ND=3&adjacent=true&locale=en_EP&FT=D&date=19980728&CC=US&NR=578

Al menos un mónomero etilénicamente insaturado, polimerizable por adición	Se polimeriza por adición con grupos etilénicos (Col. 1, líneas 13 a 21).	Se polimeriza con metacrilatos por fotoiniciación (Col. 2, líneas 47 a 61).
Al menos un polímero soluble en un disolvente no reactivo	Se emplean esteres de celulosa (Col. 1, líneas 13 a 21).	Se emplea butirato acetato de celulosa (Col. 2, líneas 47 a 61).
Al menos un solvente no reactivo	Se emplea acetona como solvente (Col. 8, líneas 15 a 24).	Se emplea acetato y alcohol como solvente (Col. 2, líneas 47 a 61).

De acuerdo con la tabla anterior, las características esenciales de la composición de la reivindicación 1 habían sido divulgadas previamente en los documentos D1 y D2, por lo tanto, la materia reivindicada no es nueva.

La reivindicación dependiente 2 no menciona alguna característica que hagan nueva la composición de la reivindicación 1, por lo cual se considera que no es nueva, ya que D1 divulga met(acrilato) de uretano reactivo y un plastificante como el dioctil adipato (Col. 7, líneas 25 a 28, Col. 9, línea 63).

Las reivindicaciones dependientes 3 y 5 no mencionan alguna característica que hagan nueva la composición de la reivindicación 1, por lo cual se considera que no son nuevas, ya que D1 divulga metacrilato uretano, metacrilato de hidroxietilo, metacrilato de etilo y tetrahidrofurfurilo para realizar la polimerización (Col. 8, línea 2, Col. 7, líneas 7 a 24).

Las reivindicaciones dependientes 3 y 4 no mencionan alguna característica que hagan nueva la composición de la reivindicación 1, por lo cual se considera que no son nuevas, ya que D2 divulga metacrilato de hidroxipropilo y metacrilato de etilo para relizar la polimerización (Col. 4, líneas 45 a 46).

Nivel inventivo (Art 18 D486)

La reivindicación 6 consiste en "*la composición polimerizable de conformidad con la reivindicación 3, caracterizada porque…*" (Ver Fl. 6 del Rad. N° 12-056629-00004-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características **esenciales**	**D1**	**D2**
Composición polimerizable de conformidad con la reivindicación 3, caracterizada porque	Composición polimerizable (Col. 1, líneas 13 a 21).	Composición polimerizable (Col. 2, líneas 47 a 61).
El monómero etilénicamente insaturado es metacrilato de hidroxipropilo.	No se menciona	Se emplea metacrilato de hidroxipropilo (Col. 4, líneas 45 a 46).
El monómero reactivo es metacrilato de hidroxietilo	Se emplea metacrilato de hidroxietilo (Col. 8, línea 2).	No se menciona

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 6, porque divulgan composiciones porimerizables como recubrimientos de uñas.

La diferencia entre la invención, definida en la reivindicación 6 y la composición del documento D1 consiste en que D1 no menciona el metacrilato de hidroxipropilo.

La diferencia entre la invención, definida en la reivindicación 6 y la composición del documento D2 consiste en que en D2 no se menciona el metacrilato de hidroxietilo.

No se evidencia algún efecto técnico que logre la diferencia porque la solución de la presente solicitud posee las mismas características de recubrimiento de uñas reveladas en el documento D1.

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así "¿cómo obtener un recubrimiento alternativo al revelado en el documento D1?".

> Sin embargo, el metacrilato de hidroxipropilo, ya está divulgado en el documento D2 que se refiere a una composición para el recubrimiento de uñas (Pág. 5, líneas 13 a 24, Pág. 8, línea 21 a Pág. 9, línea 7).

En consecuencia, una persona normalmente versada en la materia incluiría el metacrilato de hidroxipropilo de D2 en la composición de la anterioridad D1, esperando con certeza lograr el método, como la de la reivindicación 6 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Puesto que las reivindicaciones dependientes 7 a 37 no mencionan características adicionales que hagan inventiva la solicitud, se considera que tales reivindicaciones tampoco tienen nivel inventivo, ya que D1 divulga metacrilatos de propileno o etileno glicol, aminas terciarias como aceleradores para fotoiniciación, esteres de celulosa especialmente el acetato butirato o acetato propionato de celulosa, en donde se tiene una concentración del éster de celulosa entre el 5 al 95%, metacrilatos como el de tetahidrofurfurilo o etilo, pigmentos como colorantes, un metacrilato de uretano como el Ebecryl 220 que tiene un peso molecular de 770 g/mol, un solvente como la cetona que puede estar en un 70% en peso de la composición y fotoiniciadores que pueden estar en un 20% en peso en la composición (Col. 7, líneas 14 y 15, Col. 8, líneas 44 a 59, Col. 5, líneas 21 a 25, Col. 5, líneas 35 a 50, Col. 8, líneas 63 a 65, Col. 7, líneas 7 a 11, Col. 9, líneas 5 y 6, Col. 8, líneas 66 a 67). Asimismo D2 divulga fotoiniciadores como el bencil dicetal (Col. 5, líneas 3 y 4) y siendo implícito para la persona versada en la materia el empleo de sílice fumante modificada por siloxanos[4], poliamidas que modifican el endurecimiento[5] y gliceril dimetacrilato piromelitico PMGDM[6] en composiciónes polimerizables por curado.

Conclusión:
Las reivindicaciones 6 a 37 cumplen el requisito de novedad (Art. 16), pero no cumplen con el requisito de nivel inventivo (Art. 18).

8. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 5985951	1, 2, 3 y 5	Novedad/ Nivel inventivo
		6 a 37	Nivel inventivo
D2	US 5785958	1, 3 y 4	Novedad/ Nivel inventivo
		6 a 37	Nivel inventivo

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[4] Synthesis and Characterization of Chlorinated Bisphenol-Based Polymers and Polycarbodiimides as Inherently Fire-Safe Polymers. U.S. Department of transportation. 2000. Pág. 13, Párr. 3, líneas 19 y 20.

[5] Weinmann, et al. Amine-Functional Curatives for Low Temperature Cure Epoxy Coatings. Resolution Performance Products. 2001. Pág. 11, Párr. 1 a Párr. 3.

[6] Van Landuyt et al. Systematic review of the chemical composition of contemporary dental adhesives. Biomaterials. 2007. Vol. 28. Págs. 3760 y 3761. Tabla 1.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.

JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2013-07-30

Elaboró: Jorge Eduardo Cortazar Gomez
Revisó: Rosa Patricia Tellez Chavarro

tech paper

Amine-Functional Curatives for Low Temperature Cure Epoxy Coatings

By
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RESOLUTION
PERFORMANCE PRODUCTS

Abstract

An active area of technology development at Resolution Performance Products LLC (RPPLLC) is the design of improved epoxy/amine binder systems for low temperature cure coatings. Low temperature cure epoxy coatings allow applicators to extend the painting season and to increase scheduling flexibility because coating application can continue when the temperature falls below 50 °F. This paper begins with a basic overview of the curing agent technologies used for low temperature applications. The performance of several commercial low temperature curatives with standard liquid epoxy resin are studied in this work. Differential scanning calorimetry is used to monitor the cure rate at 40 °F over a 14 day period. The coatings performance in clear varnish formulations is presented; cured at standard ambient conditions (77 °F 55% R.H.) and at sub-ambient, high humidity conditions (50 °F 90% R.H. and 40 °F 80% R.H.). The study concludes with evaluation of a new approach to low temperature cure epoxy coatings. This approach uses low temperature curatives in combination with polyacrylated epoxy resins. The results show that these new binder systems give improved clarity, blush resistance and cure development under low temperature, high humidity conditions.

Introduction

In today’s competitive marketplace, formulators of epoxy/amine coatings face the dual task of meeting strict VOC regulations and improving coatings’ performance relative to historical industry standards. Traditional epoxy/polyamide coatings have served the industry well for more than 40 years but newer curative technologies eliminate some of their well-known limitations. In recent years, these new technologies have led to specialty amine hardeners for low temperature epoxy coatings. Low temperature cure coatings allow applicators to extend the painting season into the early winter months and to shorten maintenance schedules because coating application can continue even when the outside temperature falls below 50 °F.

This paper provides an overview of the curative technologies used for low temperature cure epoxy coatings. Several curatives designed for low temperature applications are evaluated in this study. We compare the performance of these curatives in unpigmented films and discuss the advantages of using DSC (Differential Scanning Calorimetry) to monitor the cure rate of epoxy/amine binder systems at low temperature. The early stages of cure are critical to blush and water spot resistance. This DSC technique measures the extent of the epoxy/amine reaction during low temperature cure. The study concludes with evaluation of a new approach to low temperature formulations. This approach uses aminefunctional curatives in combination with polyacrylated epoxy resins. The films show improved clarity, blush resistance and cure development under conditions of low temperature with high humidity.

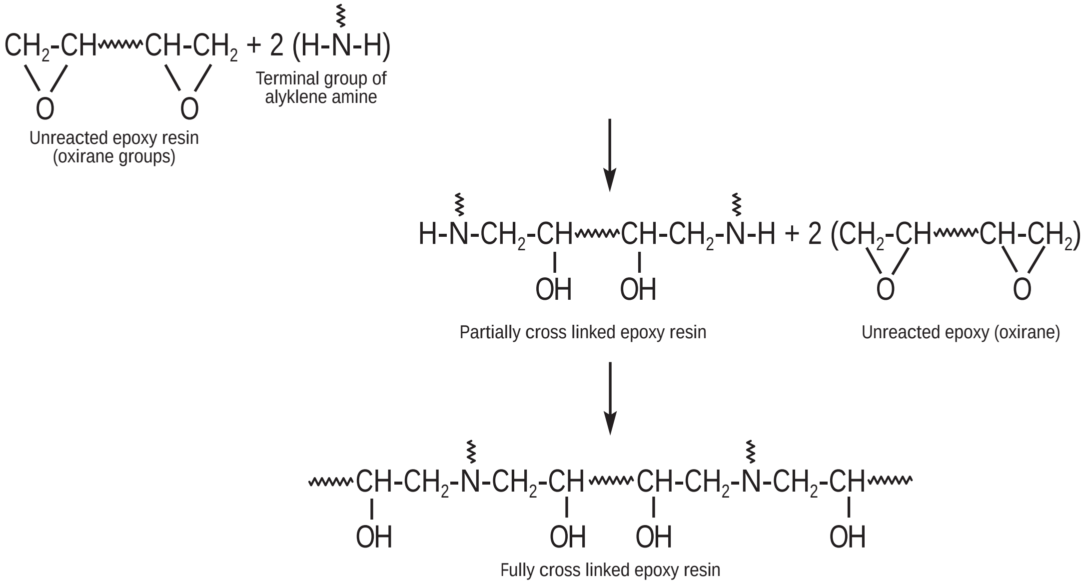
Routes to Low Temperature Cure Coatings

Epoxy/Amine Accelerators

One technology for speeding dry times and increasing the cure rate of epoxy/amine coatings for low temperature ($\leq$ 50 °F) applications is to accelerate the epoxy/amine reaction. The epoxy/amine reaction is shown in Reaction 1.

Routes to Low Temperature Cure Coatings (cont.)

Reaction 1/ **Simplified Epoxy/Amine Reaction**



Several classes of chemicals accelerate this crosslinking reaction, including organic acids (e.g., salicylic or benzoic acid), tertiary amines (e.g., BDMA - benzyl dimethyl amine, tris-2,4,6-dimethylaminomethyl phenol), alcohols (e.g., methanol), water, alkyl-substituted phenols (e.g., nonylphenol, bisphenol A) and primary aliphatic amines (e.g., DETA - diethylenetriamine, TETA- triethylene tetramine). The degree of acceleration depends on the specific chemical chosen and the concentration of active accelerator in the final formulation.

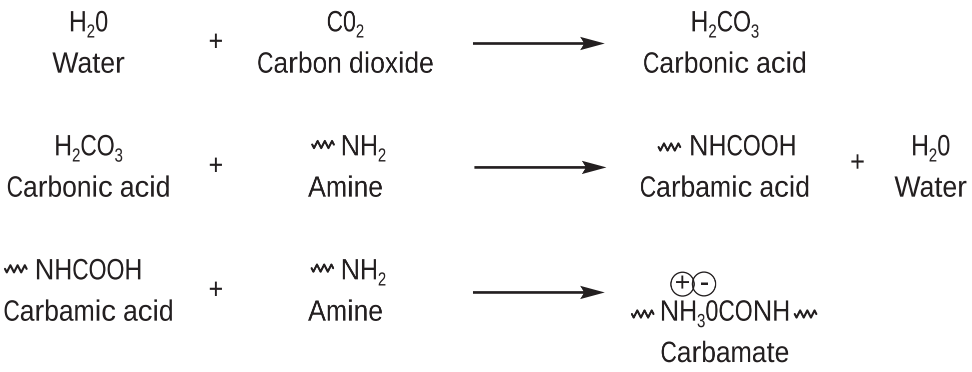
The traditional workhorse amine curatives are the polyamidoamines (or polyamides). Polyamides find applications in such diverse areas as marine, industrial maintenance, water storage and treatment, pulp and paper industry, equipment manufacture and transportation coatings. Polyamides are made by reacting dimer fatty acid with multifunctional amines such as DETA or TETA. Polyamides are generally not recommended for application at temperatures below 60 °F because of their slow reactivity. Acceptable cure rates at lower temperatures (45-55 °F) are possible if the epoxy/polyamide is accelerated with phenolic tertiary amines such as tris-2,4,6-(dimethyl aminomethyl) phenol (e.g., EPI-CURE™ Curing Agent 3253, RPPLLC; DMP-30, Rohm and Haas Co.). However, accelerator concentrations in the film must be minimized if ultimate coating properties are to be maintained. Shortened pot life is another disadvantage to using accelerators in these binder systems.

Modified Amine Adducts

In addition to meeting cure rate and chemical resistance requirements, low temperature cure epoxy coatings must be designed for blush and water spot resistance. Primary amines react with atmospheric carbon dioxide and water to form carbamates that can exude to the surface and produce blush. The formation of blush (sometimes called blooming or exudate) has a detrimental effect on coating performance because it can lead to gloss reduction, increased yellowing, poor recoatability and intercoat adhesion problems. Low temperature, high humidity conditions increase the probability of blush formation. The chemical reactions which lead to carbamate formation are depicted in Reaction 2.

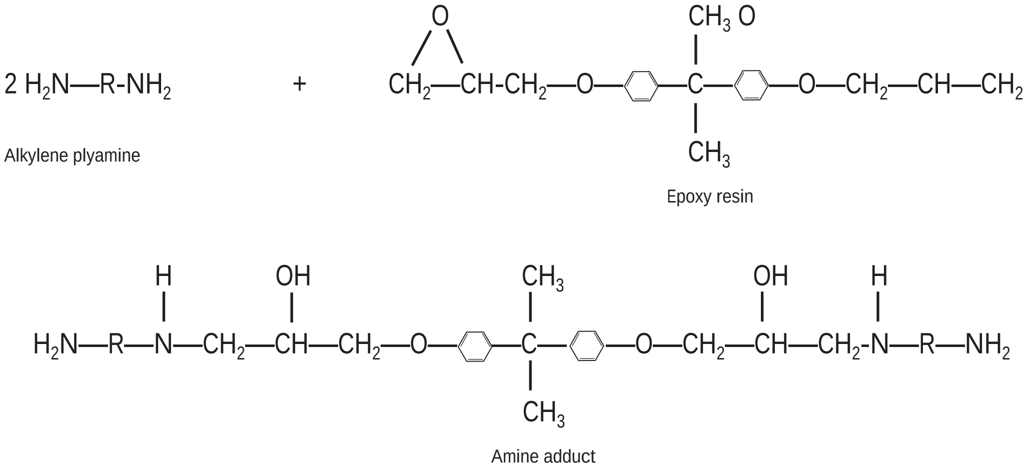
Modified Amine Adducts (cont.)

Reaction 2/**Blush Reaction: Formation of Carbamates by Amines and Moist Air**



To minimize carbamate formation and improve early water spot resistance, curing agent manufacturers have developed a wide variety of modified amine adducts. These adducts reduce or eliminate blush formation because the primary amine hydrogens are prereacted with epoxide groups. Amine adducts are prepared by reacting excess primary amines with epoxy resin. The amine adduct reaction between liquid epoxy resin and an aliphatic polyamine is depicted in Reaction 3.

Reaction 3/**Formation of Standard Amine Adduct**



A wide variety of amine curatives and epoxy resins are utilized for amine adduct reactions. Some of the most common aliphatic and cycloaliphatic amines include: diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), isophorone diamine (IPDA), bis-paraaminocyclohexyl methane (PACM) and 1,2-diaminocyclohexane (1,2-DACH). Epoxy resins used for this purpose range from liquid epoxy resins through solid epoxy resins. Since the amine adduct reaction increases molecular weight, these products are less corrosive and have lower volatility than their unmodified amine precursors. Most importantly, amine adducts are less susceptible to blush formation so they are well-suited for low temperature cure coatings. However, these advantages come at the cost of a significant

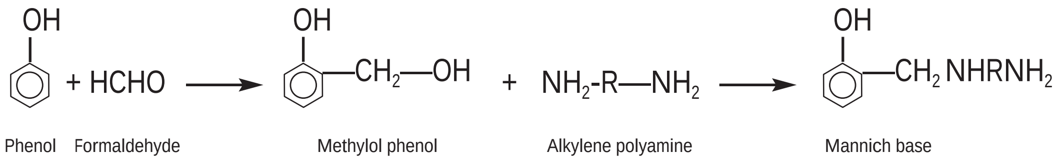
Modified Amine Adducts (cont.)

increase in curative viscosity. To lower viscosity, amine adducts are reduced with solvents or modified with plasticizers (such as benzyl alcohol). For low temperature cure, these adducts are often formulated with accelerators to further speed property development in the final coating.

Mannich Bases

These curatives are prepared by reacting amines with phenol and formaldehyde to form condensates, or Mannich bases, as they are commonly known. The reaction to form a Mannich base is depicted in Reaction 4.

Reaction 4 / **Mannich Base Reaction**



Although this reaction decreases the functionality of the amine, the presence of the phenolic hydroxyl functionality on the aromatic ring produces a substantial accelerating effect on the epoxy/amine reaction. Mannich bases cure rapidly at low temperatures (35-45 °F). They have better compatibility with epoxy resins than unmodified alkylene amines and are more resistant to blush and water spotting. In certain cases, external phenolic accelerators are added to further improve low temperature cure performance. The choice of phenol-type and amine dictate the coating film performance properties. In some cases, plasticizers are added to improve film flexibility but these plasticizers often detract from the chemical resistance of the coating film.

A naturally occuring Mannich base is 3-(n-penta8'-decenyl)phenol which is the major constituent of the oil of cashew nutshell. Using this constituent (Figure 1), several multifunctional phenalkamine curatives have been developed for low temperature cure applications. These curatives are generally darkly colored and, depending upon molecular weight, highly viscous.

Performance Survey of Low Temperature Curatives

Experimental Section

Several commercial curatives were studied to determine the performance of these products in low temperature applications. A phenalkamine curing agent (Cardolite NC541 ; Cardolite Corporation) was used as the control in this study because its low temperature performance is well-known to the industry. Curative 1 is a modified amine adduct (EPI-CURE Curing Agent 3378; RPPLLC) designed for low temperature applications. Curative 2 is a high molecular weight amine adduct supplied at 60%wt nonvolatiles in n-butanol/xylene. Low temperature epoxy coatings made from this curative have rapid hardness development with excellent solvent resistance (EPI-CURE Curing Agent 3292-FX-60, RPPLLC), Curative 3 is a phenol-free, modified Mannich base that provides fast-setting low temperature cure coatings (EPI-CURE Curing Agent 3251; RPPLLC). Their physical properties are summarized in Table 1.

Performance Survey of Low Temperature Curatives (cont.)

Figure 1/**Chemical Structure of 3-(n-penta-8'-decenyl)phenol**

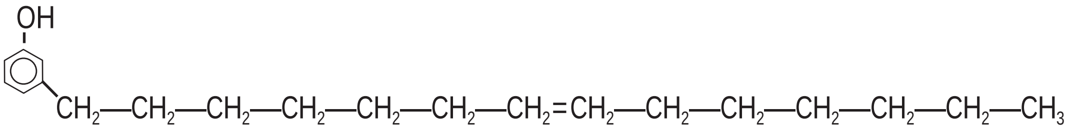


Table 1/**Physical Properties of Curatives Used in Study**

	Control (Phenalkamine)	**Curative 1** (Amine Adduct)	**Curative 2** (High Visc Adduct)	**Curative 3** (Mannich Base)
Amine value	300-335	240-265	225-257	350-390
Viscosity, cP at 25 °C	30,000	2500 cP	2500 cP	500 cP
Gardner, color	17 max.	4 max.	9 max.	5 max.
Solvent content, %w	0	0	40	0
Solvent	–	–	n-butanol/xylene	–

The first part of this study evaluates the performance of these curatives with standard difunctional liquid epoxy resin (EPON Resin 828; RPPLLC). Each binder system was mixed and reduced to Gardner H viscosity with an equal weight blend of MIBK/xylene/n-butanol. The varnish was mixed for five minutes and then applied to glass panels with a draw-down bar (1.5 mil DFT, 63 microns). After application, the coating was immediately placed in a constant temperature, constant humidity chamber. Film clarity, film tack and pencil hardness were evaluated over a two week period. Each binder system was cured using three different conditions: 77 °F, 55% R.H.; 50 °F, 90% R. H. and 40 °F, 80% R.H. The results are summarized in Table 2.

In addition to studying the performance of clear films, we monitored the rate of cure development using DSC (Differential Scanning Calorimetry). Our technique involved three steps. The first step is to run simultaneous DSC/TGA (thermog ravi metric analysis) on the mixed components (no solvent) to determine the temperature scanning range. This DSC/TGA technique shows the range of temperatures covered by the curing exotherm and sets the upper temperature limit where weight loss is still negligible (< 1 %wt).

After the temperature range was established by DSC/TGA scan (in this study, from -50 to 170 °C), a constant heating rate (10 °C/min.) DSC scan was performed to determine the total heat of reaction (ΔH_{total}) for each binder system. After reaching the upper temperature limit, the sample was quenchcooled to -50 °C and reheated to determine if any post-curing occurred and to measure the Tg of the cured system. In all cases, no post-curing was observed during the second scan.

Performance Survey of Low Temperature Curatives (cont.)

Table 2/Property Development with Liquid Epoxy Resin[1]

	Control (Phenalkamine)	**Curative 1** (Amine Adduct)	**Curative 2** (High Mw[2] Adduct)	**Curative 3** (Mannich Base)
CURE CONDITIONS: 77 °F and 55% R.H.				
Solids content, % wt (theory)	81	85	65	88
Mix ratio, phr	72	60	124	40
Shyodu gel time (100 gm)	49 min.	21 min.	63 min.	13 min.
Thin film, dry times				
Set to touch, hrs.	0.5	1.25	1.25	0.75
Cotton free, hrs.	4.75	3.5	2.75	1.75
Thru-dry, hrs.	6.75	5.75	5.0	4.25
Days to clear film	1	1	1	1
Days to tack-free film	1	1	1	1
Pencil hardness (ASTM D 3363)				
1 day	4	F	HB	F
5 days	B	F	F	F
7 days	HB	F	F	F
14 days	F	H	F	F
CURE CONDITIONS: 50 °F and 90% R.H.				
Days to clear film	14 (w/Sl. haze)	1	1	1
Film tack[2]				
1 day	Sl. tack	Tack-free	Sl. tack	Tack-free
3 days	Tack-free		Tack-free	
Pencil hardness (ASTM D 3363)				
1 day	6B	5B	6B	4B
5 days	5B	B	4B	HB
7 days	4B	B	B	F
14 days	3B	HB	HB	F
CURE CONDITIONS: 40 °F and 80% R.H.				
Pot life @ 40 °F (hrs to double initial viscosity)	2.5	2.5	3.0	2.5
Days to clear film	14 (w/haze)	3	1	5 (w/Sl. blush)
Film tack[3]				
1 day	M tack	M. tack	M. tack	Sl. tack
3 days	Sl. tack	Sl. tack	Tack-free	Tack-free
5 days	Tack-free	Tack-free		
Pencil hardness (ASTM D 3363)				
1 day	<6B	<6B	<6B	<6B
5 days	<6B	4B	5B	2B
7 days	5B	3B	4B	2B
14 days	3B	2B	4B	B

[1] EPON™ Resin 828
[2] Mw = Molecular weight
[3] Film tack: Sl = slight, M = moderate; V = very

Performance Survey of Low Temperature Curatives (cont.)

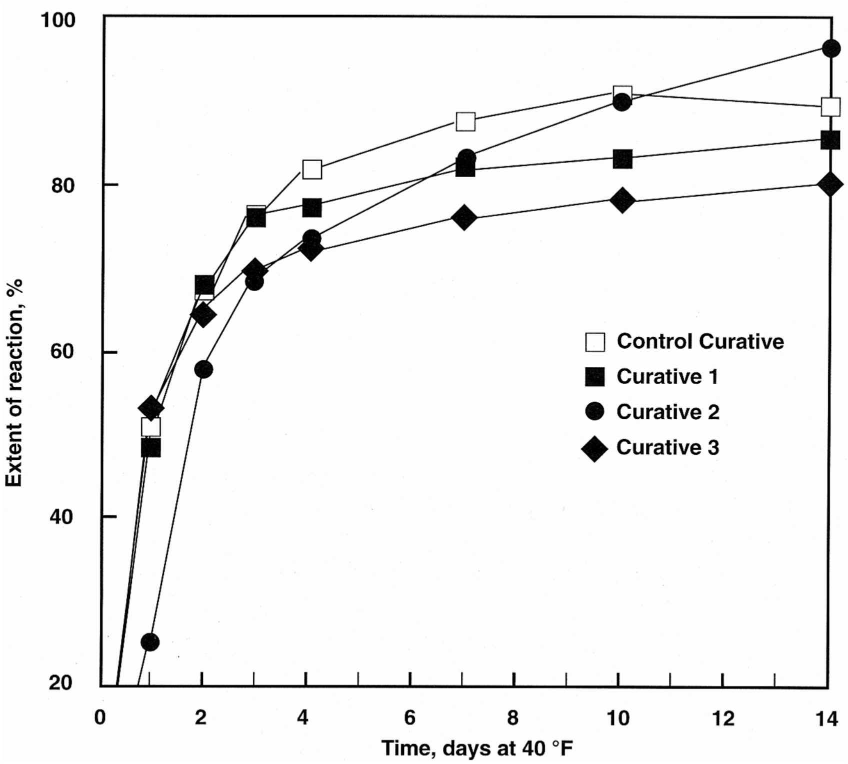
The final step of analysis was to load a freshly mixed sample into a DSC cell and immediately freeze the sample to -130 °C; while waiting for all seven samples to be prepared. Total preparation time for these seven samples was less than five minutes. The sealed DSC cells were stored at 40 °C in a refrigerator for a specific number of days (1, 2, 3, 4, 7, 10 and 14). On the appropriate day, a sample was removed and immediately scanned by DSC using a 10 °C/min. temperature ramp. The %cure for each sample measured by DSC was calculated by using Equation 1.

Equation 1:

$$\text{Extent of reaction, \%} \left[1 - \left(\frac{\Delta H\ \text{residual}}{\Delta H\ \text{total}}\right) * 100\right]$$

The results of this DSC study are summarized in Figure 2.

Figure 2/**Cure Development with Liquid Epoxy Resin (EPON™ Resin 828) at 40 °F**



Performance Survey of Low Temperature Curatives (cont.)

Observations/Conclusions (with difunctional liquid epoxy resins)

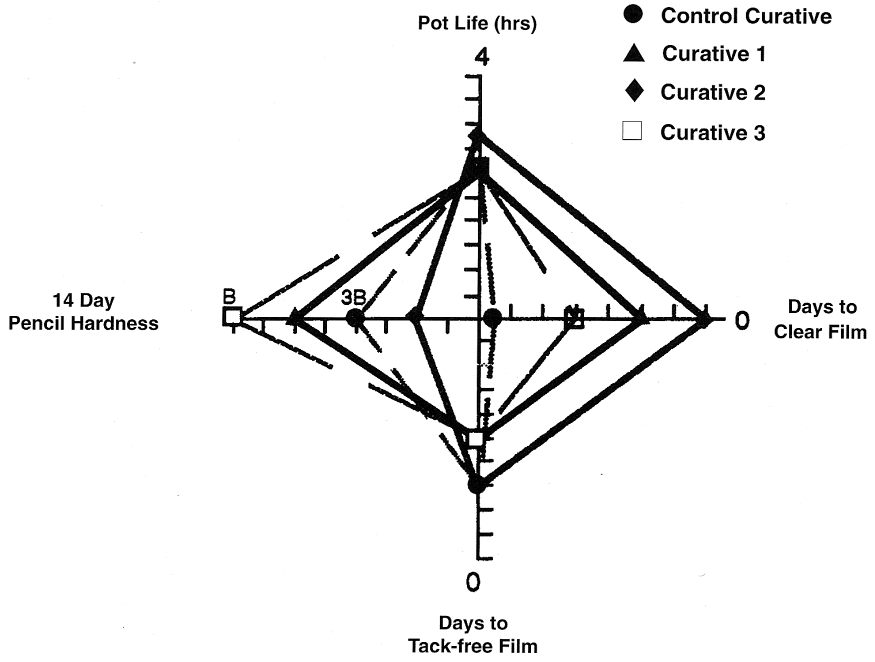
Under standard ambient conditions (77 °F and 55% R. H.), we find that each curative yields coatings with fast dry times and relatively short gel times. Acceptable pot life in fast reacting systems is a practical concern for coatings applicators. Curative 3 has the highest reactivity as demonstrated by its short gel time when combined with liquid epoxy resin (no solvent). Curative 2 has the longest gel time but this system contains solvent which slows down the reactivity. Curative 2 is a solid in the absence of solvent, so a true measure of its gel time is impractical. To better understand the relative reactivities of these curatives, the clear varnish-formulations (reduced to Gardner H viscosity) were cooled to 40 °F in an ice/water bath. Initial Brookfield viscosities at 40 °F ranged from 1200 cP-1500 cP. At 40 °F, each binder system required 2.5-3.0 hours for the varnish to double its viscosity. These results show that these curatives will have similar pot lives in high solids formulations.

At 50 °F and 90% relative humidity, each curing agent gives good tack-free times and clarity development but some differences become apparent. Film clarity and film hardness development in clear enamels based on Curative 3 are superior to the other curatives tested in this study. The tack-free time for Curative 3 is longer than that for Curative 1 but acceptable for many applications. Curative 1 gives overnight tack-free films with good ultimate film hardness. The phenalkamine control gives acceptable tack-free times but film hardness, even after 14 days, is significantly softer than the film hardness of the other curatives.

At 40 °F and 80% R.H., each curative has its own particular strengths and limitations which might influence selection of one curative versus another depending on the requirements of a specific application. In clear formulations, ultimate film clarity and blush resistance are very important properties but in pigmented formulations, other properties such as film hardness and tack-free times may be more important. To address these types of situations, a powerful graphing technique called “spider graphs” or “radar graphs” is available in today’s spreadsheet software packages. The axes in spider graphs are oriented so that better performance gives a longer ray; therefore, binders with more balanced performance have a larger area enclosed by their polygon. The performance of these curatives at 40 °F is summarized in Figure 3.

Performance Survey of Low Temperature Curatives (cont.)

Figure 3/**Performance of Low Temperature Curatives (with EPON™ Resin 828) at 40 °F and 80% Relative Humidity**



Observations/Conclusions (with difunctional liquid epoxy resins) (cont.)

The DSC technique used in this study is a powerful tool for studying the extent of reaction in low temperature coatings. When cured with the standard liquid resin, the curatives in this work give excellent cure development at 40 °F. To illustrate this, we have compared the performance of these low temperature curatives to the performance of polyamide curatives. The cure rate of two polyamide curatives (accelerated and non-accelerated) was determined at 40 °F using a similar DSC technique[1]. The data show that the extent of reaction on the third day ranged from 33-43% and after 14 days, the extent of reaction was only 55-65% complete. With the low temperature curatives in this study (Figure 2), the extent of reaction at three days ranged from 65-75% and after 14 days, the extent of reaction ranged from 75-95% complete.

The DSC work, combined with the performance in clear enamels, demonstrates that these aminefunctional curatives have excellent reactivity under low temperature, high humidity conditions. The superior cure development of these curatives, compared to polyamides, is most evident in the initial stages of cure when development of coating properties is most critical. As the extent of reaction increases, properties such as chemical resistance, corrosion resistance and tensile strength increase accordingly.

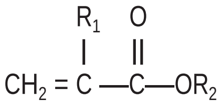
Curative 2 had the initial cure rate during the first four days but, after 14 days, it had the highest extent of reaction. Although the curatives in this study have excellent cure response at low temperatures, other performance testing[2] demonstrates that each curative is best suited for particular applications. RPPLLC recommends Curative 2 for industrial maintenance primers, marine primers and solvent-resistant tank linings. Curative 1 has excellent water resistance

Performance Survey of Low Temperature Curatives (cont.)

Observations/Conclusions (with difunctional liquid epoxy resins) (cont.)
and good corrosion resistance so it is recommended for waste water coatings and solvent-free marine coatings. The high reactivity of Curative 3 and its excellent chemical resistance makes this curative a candidate for use in chemical ly-resistant tank linings, synthetic flooring applications and as a co-curing agent for polyamide-based coatings.

Improved Binder Systems for Low Temperature Cure

Although these curatives have good performance with difunctional liquid epoxy resin, even under low temperature, high humidity conditions, an improved binder system can be developed by replacing the standard liquid epoxy resin with low viscosity epoxy/polyacrylate resins. These resins are based on liquid epoxy resin that has been modified with multiacrylate esters. By tailoring the amount and type of modification, a wide range of resin reactivities can be obtained in the final film (Table 4). Acrylate esters are represented by the general formula:



$$CH_2 = \overset{\overset{R_1}{|}}{C} - \overset{\overset{O}{\|}}{C} - OR_2$$

R_1 = H or CH_3

R_2 = H or alkyl

Table 4/**Physical Properties of Polyacrylated Epoxy Resins**

	Polyacrylated Epoxy One[1]	Polyacrylated Epoxy Two[2]	Polyacrylated Epoxy Three[3]	Polyacrylated Epoxy Four[4]
Viscosity, cP @ 25 °C	2180	950	700	110
Shyodu gel time (w/ EPI-CURE™ Curing Agent 3271)	7 min.	1 min.	5 min.	5.5 min.
Equivalent wt, by reaction with amine	177	140	192	150
WPE	210	310	220	315

[1] EPON™ Resin 8161 (RPPLLC)
[2] EPON Resin 8111
[3] EPON Resin 8101
[4] EPON Resin 8021

The nature of the R groups determine the properties of each monomeric ester and the polymers derived from it. Aliphatic primary amines add rapidly across the acrylate double bond in a Michael's addition reaction. Secondary amines do not react well with the acrylic modifications. For this reason, aliphatic amines and cycloaliphatic amines are recommended for use with polyacrylated epoxy resins but amidoamines and polyamides are generally not recommended as hardeners for these resins.

In the second phase of this study, we examined the performance of Polyacrylated Epoxy Four with the low temperature curatives studied earlier. Using the procedures described in the Experimental Section, we applied the binder varnishes to glass panels and cured them in the environmental chamber. The results of this testing are summarized in Table 5.

Improved Binder Systems for Low Temperature Cure (cont.)

Table 5/**Film Properties With Polyacrylate-modified Liquid Epoxy Resin**[1]

	Control (Phenalkamine)	**Curative I** (Amine Adduct)	**Curative 2** (High Mw[2] Adduct)	**Curative 3** (Mannich Base)
CURE CONDITIONS: 77 °F and 55% R.H.				
Solids content, % wt (theory)	85	95	67	100
Mix ratio, phr	90	76	155	51
Shyodu gel time (100 gm)	43 min.	18.5 min.	27 min.	5 min.
Thin film, dry times				
Set to touch, hrs.	1.25	1.25	1.25	0.5
Cotton free, hrs.	3.5	4.0	3.5	1.25
Thru-dry, hrs.	13.5	6.0	5.25	1.75
Days to clear film	1	1	1	1
Days to tack-free film	4	2	1	1
Pencil hardness (ASTM D 3363)				
1 day	<6B	4B	F	HB
5 days	5B	2B	F	F
7 days	3B	HB	F	F
14 days	2B	F	F	F
CURE CONDITIONS: 50 °F and 90% R.H.				
Days to clear film	3	1	1	1
Film tack[3]				
1 day	Tacky	M. tack	Tack-free	Tack-free
3 days	M. tacky	Tack-free		
5 days	Tack-free			
Pencil hardness (ASTM D 3363)				
1 day	<6B	<6B	4B	B
5 days	5B	6B	HB	HB
7 days	3B	HB	F	F
14 days	HB	HB	F	F
CURE CONDITIONS: 40 °F and 80% R.H.				
Pot life @ 40 °F (hrs to double initial viscosity)	1.0	0.75	1.5	0.25
Days to clear film	3	3	1	3
Film tack[3]				
1 day	V. tacky	Tacky	Tack-free	Tack-free
3 days	Tacky	Tack-free		
5 days	Sl. tacky			
7 days	Tack-free			
Pencil hardness (ASTM D 3363)				
1 day	<6B	<6B	<6B	<6B
5 days	<6B	5B	F	HB
7 days	<6B	4B	F	F
14 days	4B	2B	F	F

[1] EPON™ Resin 8021

[2] MW = Molecular weight

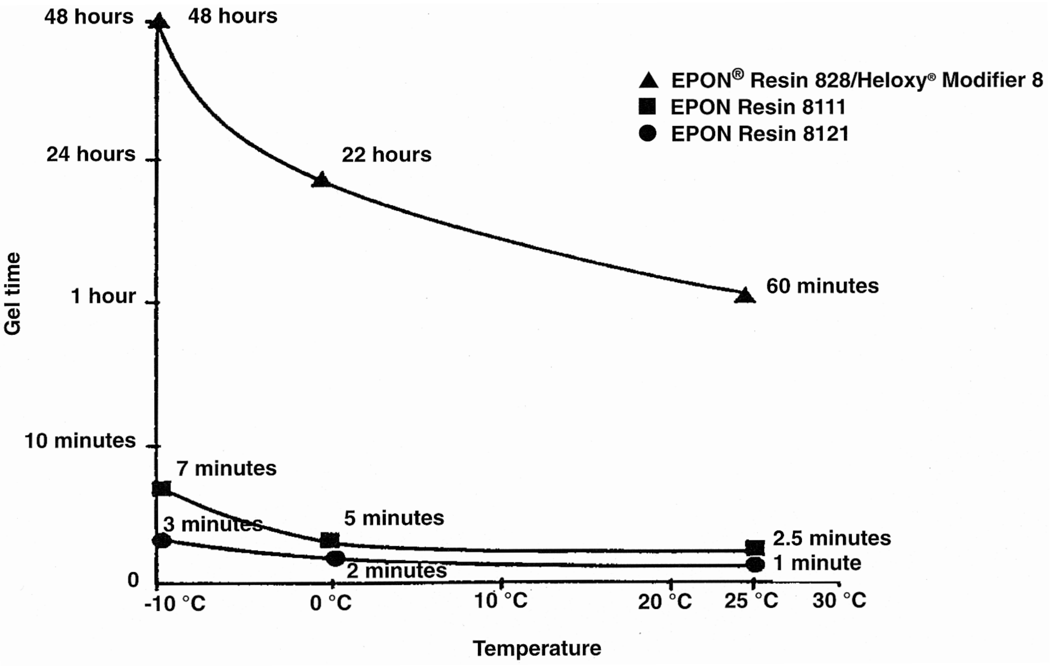
[3] Film tack: Sl = slight; M = moderate, V = very

Improved Binder Systems for Low Temperature Cure (cont.)

Observations/Conclusions (with polyacrylated epoxy resins)

Polyacrylated epoxy resins, in combination with these low temperature curatives, show significant advantages over standard liquid epoxies in low temperature, high humidity conditions. The significant improvements in the rate of film hardness, blush resistance, and clarity come from the rapidity of the Michael's addition reaction. A unique feature of epoxy polyacrylates is that their reactivity is relatively independent of temperature effects3. (See Figure 4).

Figure 4/**Polyacrylated Epoxy-amine Reactivity versus Temperature**



The advantage of this unique reactivity in low temperature applications is that the cure rate of polyacrylated epoxy resin is less affected by temperature than the cure rate of standard liquid epoxy resins. Polyacrylated epoxy resins bring two additional advantages to low temperature coating applications: increased blush resistance at high humidity and low viscosity for high solids or solventless formulations.

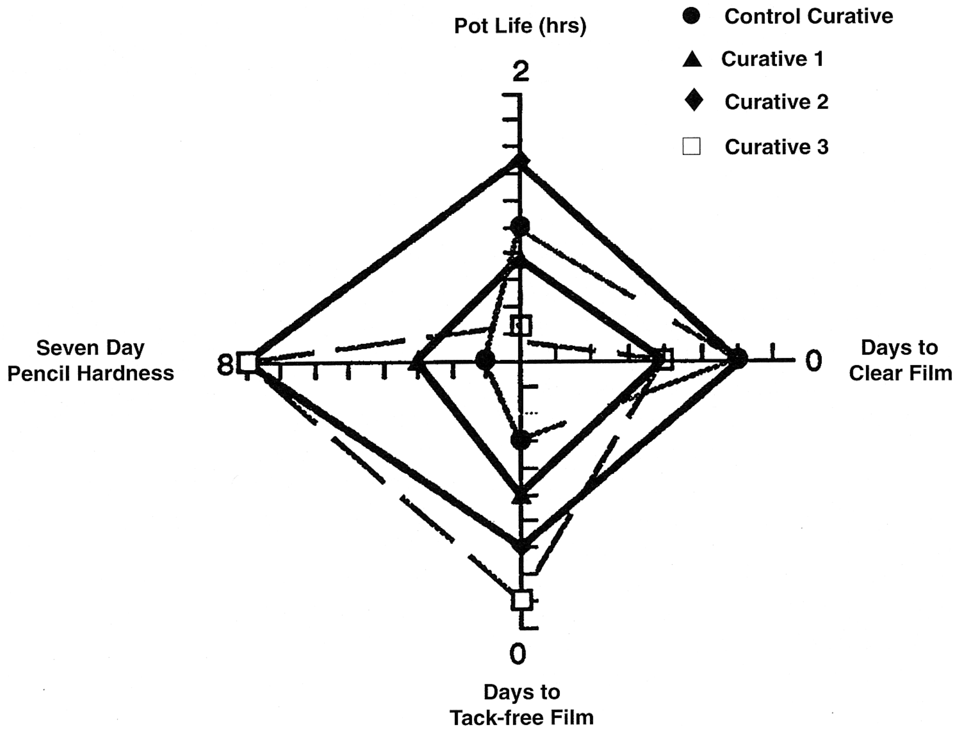
The gel times for these binder systems are very short, as shown in Table 5. For example, Curatives 2 and 3 have gel times which are shorter than the gel times with standard liquid epoxy resin (Table 2) by a factor of two. The Control and Curative 1 also have shorter gel times but the difference is not as dramatic (e.g., Curative 1/Polyacrylate Epoxy: 18 minute gel, Curative 1/Standard Epoxy: 21 minute gel time).

The higher reactivity is also reflected in faster thin film set times for room temperature applications. Curative 3 is particularly interesting because its thrudry time drops from 4.25 hours with standard liquid epoxy down to only 1.75 hours with Polyacrylated Epoxy Four. Faster dry times are the key reason that these resins are used extensively in flooring and adhesive applications. Other applications for fast dry epoxy resin systems include auto refinish, railcar applications, and OEM coatings.

Improved Binder Systems for Low Temperature Cure (cont.)

Observations/Conclusions (with polyacrylated epoxy resins) (cont.)
Even at low temperature, the pot life of these systems is unacceptably short for standard application equipment. However, the low viscosity of these systems is perfectly suited for plural component, solventless equipment which is gaining acceptance in many shop-based applications. Since the binder viscosity is low, heated plural component equipment may not be required. Two formulation alternatives for longer pot life are to either blend standard epoxy resin with the polyacrylated resin to decrease reactivity or choose alternative aliphatic amines which are less reactive than the low temperature curatives described in this study. The binder system based on Curative 2/Polyacrylated Epoxy Resin Four is unique because it has a pot life of 1.5 hours at 40 °F with fast clarity and hardness development. The performance of each binder system at 40 °F is summarized in Figure 5.

Figure 5/**Performance of Low Temperature Curatives with Polyacrylate-modified Liquid Epoxy Resin (EPON Resin 8021) at 40 °F and 80% Relative Humidity**

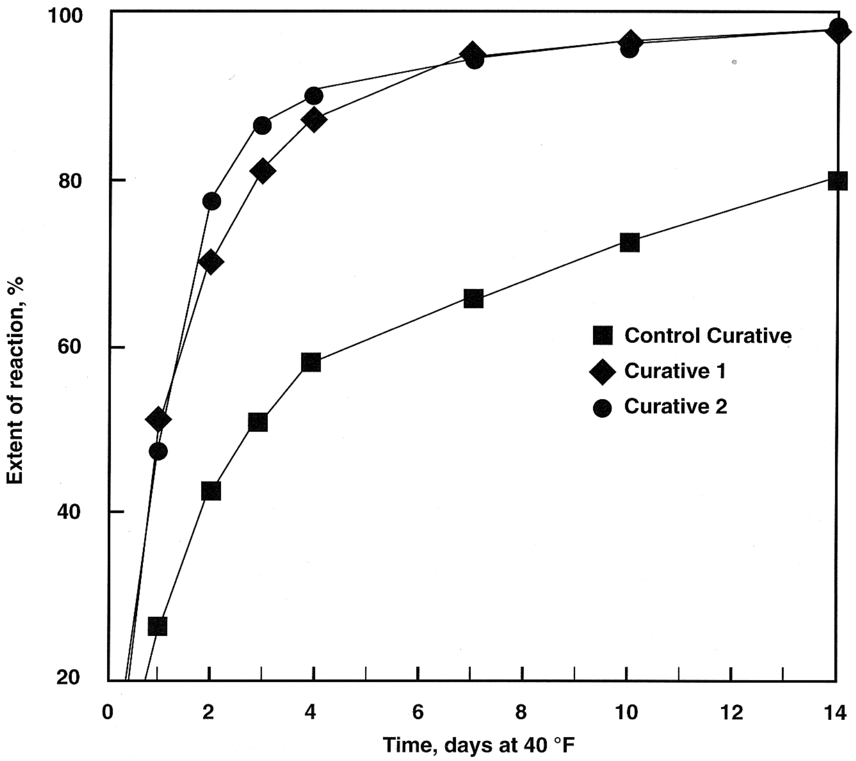


The long tack-free times and slow hardness development in the Control Curative and Curative 1 show that these curing agents may not be suitable for use with Polyacrylated Epoxy Four. These results suggest that these curatives have a low primary amine content. Since Polyacrylated Epoxy Four has a high level of modification, an alternative polyacrylated epoxy resin with lower modification (such as Polyacrylated Epoxy Three) might be a more suitable epoxy resin for these curatives.

In addition to the film performance, we determined the cure rates of these new binder systems using the DSC technique described earlier. Curative 3 was not included in this study because the reactivity of the binder at 40 °F was too fast to allow accurate determination of the ΔH_{total}. The results of this DSC study are summarized in Figure 6.

Improved Binder Systems for Low Temperature Cure (cont.)

Figure 6/**Cure Development with Polyacrylated Epoxy Resin (EPON™ Resin 8021) at 40 °F**



The figure indicates that binders based on Curatives 1 and 2 have a very fast rate of cure during the first few days after application. The Control curative has a much slower cure rate. It eventually reaches a reasonable degree of crosslinking but the film hardness is unacceptably soft (4B after 14 days).

Compared to standard liquid epoxy resin, the extent of reaction for these binder systems is comparable but the clear films have significantly better blush resistance and clarity development. The dry times of the polyacrylated resins are also greatly improved relative to standard liquid epoxy resin. The one drawback of these new binder systems is that the pot life is significantly shorter than standard liquid epoxy resin.

Summary

This paper summarizes recent efforts to evaluate epoxy/amine binder systems for low temperature cure coatings. The first section reviews the curing agent technologies used for these applications. Several commercial ly-available low temperature curatives were evaluated with standard liquid epoxy resin in clear varnish formulations to determine their film performance under different cure conditions: 77 °F and 50% R.H., 50 °F and 90% R.H., 40 °F and 80% R. H. A DSC (Differential Scanning Calorimetry) technique is discussed in detail which measures the extent of reaction during the critical early cure period. Polyacrylate-modified liquid epoxy resins have been used for several years in the flooring industry for their superior low temperature reactivity. This study evaluates the performance of a standard polyacrylate-modified liquid epoxy resin with these low temperature curatives, The results of this study demonstrate that these new binder systems have significantly better clarity, blush-resistance and hardness development than comparable systems based onstandard liquid epoxy resin. Based on the positive results from this study, additional work is being started to determine the performance of these binder systems in fully-pigmented starting point formulations.

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Review

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.

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

Contents

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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 of residual double bonds (–C=C–) in the oxygen inhibition layer. As for the bond to enamel and dentin, micromechanical adhesion is assumed to be the prime bonding mechanism [3]. This is achieved by an exchange process by which inorganic tooth material is replaced by resin monomers that become interlocked in the retentions upon curing [4,5]. Diffusion and capillarity are the primary mechanisms to obtain micro-mechanical retention. Microscopically, this process is called 'hybridization' [6]. Whereas this process entails simple interlocking of resin in etch-pits in enamel, entanglement of resin within the exposed collagen lattice occurs in dentin. However, recent self-etch adhesives with a mild (relatively high) pH do not completely expose collagen anymore. An additional mechanism of ionic bonding of acidic monomers and calcium in hydroxyapatite was recently established [7], which may explain the good clinical performance of some of these mild self-etch adhesives [8].

Considering these underlying bonding mechanisms, one can define some requirements for adhesive systems. Micromechanical interlocking will occur after consecutive demineralization, resin infiltration and polymer setting. As a consequence, adequately removing the smear layer together with demineralizing enamel and dentin to a small extent, good wetting, diffusion, penetration and good polymerization of the resin components are all important. Chemical bonding can be achieved by adding specific monomers with affinity for hydroxyapatite. Last, sufficient 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

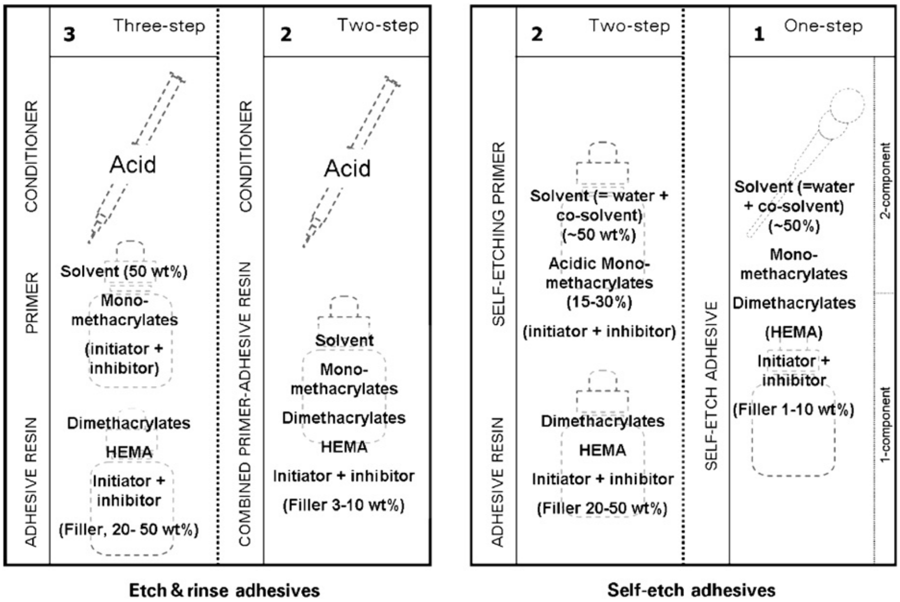


Fig. 1. Classification of contemporary adhesives according to Van Meerbeek et al. [5]. Even though most adhesives contain the same components, they may differ significantly considering the proportional amount of ingredients. As indicated, most adhesives contain methacrylate-based monomers. The mentioned percentages of ingredients are approximations; nevertheless a lot of variation considering the proportional composition of adhesives exists between different products. Two-step etch&rinse adhesives are often referred to as 'one-bottle'systems. Irrespective of the classification, each component, either primer or bonding or self-etching adhesive can come in two bottles that need to be mixed prior to application. As such, one-step self-etch adhesives are often subdivided in one- and two-component systems.

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 –C=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 [10,10–14]. 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 (R_1–CO–OR_2) [20]. A new group of monomers, methacrylamides, was designed to overcome these problems (Fig. 2). Methacrylamides have an amide group (R_1–CO–NH–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

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
Three-step etch&rinse adhesives (3-E&R)					
Adper Scotchbond Multi-Purpose	3M ESPE, St Paul, MN, USA	*Component 1(etchant)*: 35% H_3PO_4 *Component 2*: (Scotchbond Multi-Purpose primer) HEMA, polyalkenoic acid polymer, water *Component 3*: (Scotchbond Multi-Purpose adhesive) Bis-GMA, HEMA, tertiary amines (both for light-cure and self-cure initiators), photo-initiator	Primer: 3.3 Bonding: 8.2		
Adper Scotchbond Multi-Purpose Plus	3M ESPE, St Paul, MN, USA	*Component 1 (etchant)*: 35% H_3PO_4 *Component 1,5*: (Scotchbond Multi-Purpose Plus activator) ethanol, sulfinic acid salt, sodium salt *Component 2*: (Scotchbond Multi-Purpose primer) HEMA, polyalkenoic adic polymer, water *Component 3*: (Scotchbond Multi-Purpose adhesive) Bis-GMA, HEMA, tertiary amines (both for light-cure and self-cure initiators), photo-initiator *Component 3,5*: (Scotchbond Multi-Purpose Plus catalyst) Bis-GMA, HEMA, BPO	Comp 1,5: 8,1 Comp 2: 3,3 Comp1,5 +comp 2: 4,7 Comp 3: 8,2 Comp 3,5: 5,7 Comp 3,5+comp 3: 6,9	Dual cure	
All-Bond 2	Bisco Inc, Schaumburg, IL, USA	*Etchant*: 10% H_3PO_4 (All-etch) or 32% H_3PO_4 (Uni-etch) *Primer A*: NTG-GMA, acetone, ethanol, water *Primer B*: BPDM, photo-initiator, acetone *Bonding*: Bis-GMA, UDMA, HEMA *Pre-Bond*: Bis-GMA, TEGDMA, BPO, HEMA	Primers mixed: 5.7 Bonding: 7.5 Pre-bond: 7 Pre-bond+bonding: 7	Dual cure primer Dual cure bonding when mixed with Pre-bond	Wet
Bond-it	Pentron Corporation, Wallingford, CT, USA	*Etchant*: 37% H_3PO_4 *Primer A*: NTG-GMA, acetone *Primer B*: PMGDM, Bis-GMA, HEMA, acetone, photo-initiator *Adhesive resin*: Bis-GMA, HEMA, UDMA, HDDMA with amine accelerator, photo-initiator, BPO		Light cure (or dual cure when activator is added)	Wet bonding
Clearfil Liner Bond	Kuraray Medical Inc, Tokyo, Japan	*Etchant*: K-etchant *SA primer*: 5-NMSA, ethanol, water *Photo bond*: *Catalyst liquid*: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, BPO, CQ *Universal liquid*: *N*,*N*′-diethanol p-toluidine, sodium benzen sulfinate, ethanol			
Ecusit-Primer/ Mono	DMG, Hamburg, Germany	*Ecusit-Etch*: 37% H_3PO_4 *Primer*: maleic acid, HEMA, polymethacrylated polycarbonic acid *Bonding*: Bis-GMA, TEGDMA, polymethacrylated oligomaleic acid	2.6	Light cure	Preferentially moist
FL bond (Imperva Fluorobond in Japan)	Shofu Inc., Kyoto, Japan	*Etchant*: 7% H_3PO_4 *Primer A*: water, acetone, initiator *Primer B*: 4-AET, 4-AETA, HEMA, UDMA, TEGDMA, initiator *Bond*: F-PRG Filler, HEMA, UDMA, TEGDMA, photo-initiator	2.2	Fluoride releasing Light cure	Dry
Gluma Solid Bond		*Gluma Etch*: 20–35% H_3PO_4	1.8	Light cure	Wet

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
	Heraeus Kulzer, Hanau, Germany	*Gluma solid bond P*: TEGDMA, HEMA, modified polyacrylic acid, maleic acid, acetone, water, photo-initiators, stabilizers *Gluma solid bond S*: Bis-GMA, TEGDMA, glass filler, SiO_2, photo-initiators, stabilizers			
Optibond	Kerr, Orange, CA, USA	*Etchant*: 37.5% H_3PO_4 *Primer*: HEMA, GPDM, MMEP, water, ethanol, CQ, BHT *Dual cure activator (3A)*: Bis-GMA, HEMA, MMEP, BPO, UV-9, BHT, CQ *Dual Cure Paste (3B)*: Bis-GMA, HEMA, GDMA, DHEPT, ODMAB, filler (fumed SiO_2, barium aluminoborosilicate, barium aluminosilicate, Na_2SiF_6), coupling factor A174		Dual cure	
Optibond FL	Kerr, Orange, CA, USA	*Etchant*: 37.5% H_3PO_4 *FL Prime*: HEMA, GPDM, MMEP, water, ethanol, CQ, BHT *FL Adhesive*: Bis-GMA, HEMA, GDMA, CQ, ODMAB, filler (fumed SiO_2, barium aluminoborosilicat, Na_2SiF_6), coupling factor A174 (approximately 48 wt% filled)	FL Prime: 1.9 Fl Adhesive: 6.9	Light cure	
PAAMA	SDI limited, Bayswater, Victoria, Australia	*Etchant*: 37% H_3PO_4 *Primer*: acetone, proprietary hydrophilic/hydrophobic monomer, TEGDMA *Bonding*: UDMA, TEGDMA, stabilizers, CQ	Primer: 3.5 Bonding: 5		Wet
Probond	DENTSPLY Caulk, Milford, DE, USA	*Etchant*: H_3PO_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_3PO_4 *Primer*: HEMA, TEGDMA, maleic acid, polycarboxylic acid, ethanol, water, CQ *Bonding*: Bis-GMA, TEGDMA, silicate glass fillers, silica, polycarboxylic acid, CQ		Light cure	Dry
Solobond Plus	VOCO, Cuxhaven, Germany	*Etchant*: Vococid 35% H_3PO_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_3PO_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_3PO_4 *Adhesive*: dimethacrylates, HEMA, polyalkenoid acid copolymer, 5 nm silane treated colloidal silica, ethanol, water, photo-initiator		Light cure	Wet (blot dried surface)
Bond-1	Pentron Corporation, Wallingford, CT, USA	*Etchant*: 37% H_3PO_4 *Adhesive*: PMGDM, HEMA, TMPTMA, initiators, acetone		Light cure	
Clearfil Photobond		K-etchant		Dual cure	

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
	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_3PO_4 *Adhesive*: HEMA, phosphonic acid acrylate, Bis-GMA, dimethacrylates, silica, ethanol, catalysts, stabilizers		Light cure	
Excite DSC	Ivoclar Vivadent, Schaan, Liechtenstein	*Total Etch*: 37% H_3PO_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_3PO_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_3PO_4 *Adhesive*: UDMA, HEMA, 4-META, acetone, photo-initiators, stabilizers		Light cure	Wet
Heliobond	Ivoclar Vivadent, Schaan, Liechtenstein	*Total Etch etchant*: 37% H_3PO_4 *Adhesive*: Bis-GMA, TEGDMA, catalysts, stabilizers			Dry
One Coat Bond	Coltene-Whaledent, Altstätten, Switzerland	*Etchant*: Coltene etchant 15 (15% H_3PO_4) or Coltene etchant gel s (35% H_3PO_4) *Adhesive*: HEMA, HPMA, glycerol dimethacrylate, methacrylized polyalkenoate, UDMA, amorphous silica, CQ			
One-Step	Bisco Inc, Schaumburg, IL, USA	*Etchant*: 32% H3PO4 (Uni-etch), 37% H3PO4 (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% H3PO4 (Uni-etch), 37%H3PO4 (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_3PO_4 *Adhesive*: Bis-GMA, HEMA, GDMA, GPDM, ethanol, CQ, ODMAB, BHT, filler (fumed SiO_2, barium aluminoborosilicate, Na_2SiF_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_3PO_4 *Bottle A+B*: BIS-GMA, TEGDMA, hexandioldimethacrylate, BPO	6.9	Dual cure Enamel adhesive	

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
Prime&Bond NT	DENTSPLY De Trey, Konstanz, Germany	*Etchant*: H_3PO_4 *Adhesive*: PENTA, TEGDMA, Bis-GMA, cetylamine hydrofluoride, acetone, nanofiller (amorphous silicon dioxide 8 nm), resin R5-62-1, T-resin, D-resin, CQ			
Prime&Bond NT dual cure	DENTSPLY Caulk, Milford, DE, USA	*Self-cure activator*: aromatic sodium sulfinate, acetone, ethanol		Dual cure Needs to be mixed with Prime&Bond NT	
Quadrant Uni-1-Bond	Cavex Holland B.V., Haarlem, the Netherlands	*Quadrant Total-Etch*: 20% H_3PO_4 *Adhesive*: 4-META, Bis-GMA, HEMA, UDMA, maleic acid, polycarboxylic acid, ethanol, water, CQ		Light cure	Dry & wet
Solist	DMG, Hamburg, Germany	*Ecusit-Etch*: 37% H_3PO_4 *Adhesive*: HEMA, TEGDMA, elastomers, methacrylated phosphoric acid	2.2		Wet
Solobond M	VOCO, Cuxhaven, Germany	*Etchant*: Vococid 35% H_3PO_4 *Adhesive*: BIS-GMA, HEMA, phosphate methacrylates, BHT, acetone, CQ, amine accelerator	2.2		Wet
Stae	SDI limited, Bayswater, Victoria, Australia	*Etchant*: 37% H_3PO_4 *Adhesive*: acetone, water, proprietary hydrophilic/hydrophobic monomer, HEMA, CQ, stabilizer	3.5	Light cure	Wet
Superbond C&B	Sun Medical Co, Shiga, Japan	*Red activator* (*for enamel*): aqueous phosphoric acid, organic thickener *Green activator* (*for dentin*): aqueous citric acid, ferric chloride *Monomer*: 4-META, MMA *Catalyst*: partially oxidated tributylborane (TBB) *Polymer* (*clear*): polymethylmethacrylate	Red Activator: 1 Green Activator: 1 Cement mixture: 6	Self-cure Used as cement to bond indirect restorations to tooth surfaces Monomer, catalyst and polymer are mixed together	Dry
XP*BOND*	DENTSPLY De Trey, Konstanz, Germany	PENTA, TCB, HEMA, TEGDMA, UDMA, tert-butanol, nanofiller, CQ, stabilizer	∼2.1		Wet
2-step self-etch adhsesive (2-SEA)					
AdheSE	Ivoclar Vivadent, Schaan, Liechtenstein	*Primer*: acrylic ether phosphonic acid, bisacrylamide, water, CQ, stabilizers *Bonding*: Bis-GMA, GDMA, HEMA, fumed silica, CQ, tertiary amine, stabilizers	Primer: 1.7 Bonding: 7.7	Light cure	Dry
Clearfil Liner Bond 2 (Clearfil Liner Bond II in Japan)	Kuraray Medical Inc, Tokyo, Japan	*Primer A*: Phenyl-P, 5-NMSA, CQ, ethanol *Primer B*: HEMA, water *LB BOND*: MDP, HEMA, hydrophobic dimethacrylate, CQ, silanated colloidal silica	Mixed primer: 1.4	Light cure	
Clearfil Liner Bond 2V (Clearfil Liner Bond II Σ in Japan)	Kuraray Medical Inc, Tokyo, Japan	*Primer A*: MDP, HEMA, hydrophilic dimethacrylate, *N*-*N*-diethanol p-toluidine, photo-initiator, water *Primer B*: HEMA, hydrophilic dimethacrylate, water *Bond A*: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, CQ, silanated colloidal silica *Bond B*: HEMA, Bis-GMA, hydrophobic dimethacrylate, BPO, *N*,*N*′-diethanol p-toluidine, CQ, silanated colloidal silica	Mixed primer: 2.8	Dual cure	

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
Clearfil Protect Bond	Kuraray Medical Inc, Tokyo, Japan	*Primer*: MDPB, MDP, HEMA, hydrophilic dimethacrylate, photo-initiator, water *Bond*: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, photo-initiators, silanated colloidal silica, surface-treated NaF	2	Light cure	Dry
Clearfil SE Bond Clearfil Mega (Bond) in Japan	Kuraray Medical Inc, Tokyo, Japan	*Primer*: MDP, HEMA, hydrophilic dimethacrylate, photo-initiator, water *Bond*: MDP, HEMA, Bis-GMA, hydrophobic dimethacrylate, photo-intiators, silanated colloidal silica	2	Light cure	Dry
Contax	DMG, Hamburg, Germany	*Primer*: Maleic acid, water *Bonding*: Bis-GMA, methacrylic esters of polyalcohols, HEMA	2.6; 1.3 in water	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	Preferentially moist
Nano-Bond	Pentron Corporation, Wallingford, CT, USA	*Self-etch primer*: sulfonic acid terminated resin, HEMA, water *Adhesive*: PMGDM, HEMA, UDMA, TMPTMA, POSS nano-particulates, photo-initiator, amine accelerator, acetone *Self-cure activator*: BPO, acetone		Light cure or dual cure when activator is added	
One Coat Self Etching Bond	Coltene-Whaledent, Altstätten, Switzerland	*Primer*: water, HEMA, acrylamidosulfonic acid, glycerol mono- and dimethacrylate, methacrylized polyalkenoate *Bonding*: HEMA, glycerol mono- and dimethacrylate, UDMA, methacrylized polyalkenoate, CQ			
Optibond Solo Plus Self-etch	Kerr, Orange, CA, USA	*Self-etch primer*: HFGA-GMA, GPDM, ethanol, water, MEHQ, ODMAB, CQ *Adhesive*: Bis-GMA, HEMA, GDMA, GPDM, ethanol, CQ, ODMAB, BHT, filler (fumed SiO_2, barium aluminoborosilicat, Na_2SiF_6), coupling factor A174 (approximately 15 wt% filled)	SE primer: 1.9 Adhesive: 2.2	Light cure	
Tokuso Mac Bond II	Tokuyama Dental Corporation, Tokyo, Japan	*Self-etching primer (primer a+primer b)*: MAC-10, methacryloylalkyl acid phosphate, water, acetone *Bonding*: MAC-10, HEMA, Bis-GMA, TEGDMA, CQ			Dry
Unifil Bond	GC, Tokyo, Japan	*Primer*: 4-MET, HEMA, ethanol, water, CQ *Bonding*: UDMA, HEMA, DMA, CQ, silica			
One-step self-etch adhesive (1-SEA)					
Absolute	DENTSPLY Sankin Kogyo, Otahara, Japan	Methacrylate ester, fluoride compound, anhydrous silicic acid, acetone		Does not contain water	Wet
Admira Bond	VOCO, Cuxhaven, Germany	Ormocers, BIS-GMA, HEMA, phosphate methacrylates, BHT, acetone, CQ, amine accelerator	2.1		Wet
Adper Prompt L Pop	3 M ESPE, ST Paul, USA	*Red cushion*: Methacrylic phosphates, BIS-GMA, photo-initiator *Yellow cushion*: Water, HEMA, polyalkenoic acid polymer		Light cure	Dry

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
AQ Bond (also marketed as Touch&Bond by Parkell, USA)	Sun Medical Co, Shiga, Japan	*AQ Bond*: water, acetone, 4-META, UDMA, monomethacrylates, photo-initiator, stabilizer *AQ-sponge*: sodium p-toluenesulfinate adsorbed in polyurethane foam	2.5	Light cure Contains special ternary catalysts to enhance coupling with chemically cured resins	Dry
Clearfil S^3 Bond	Kuraray Medical Inc, Tokyo, Japan	MDP, Bis-GMA, HEMA, photo-initiators, ethanol, water, silanated colloidal silica	2.7	Light cure	Dry
Futurabond NR	VOCO, Cuxhaven, Germany	*Bottle A and B*: BIS-GMA, HEMA, phosphate methacrylates, BHT, ethanol, fluorides, CQ, siliciumdioxide nanoparticles	1.4		
G-Bond	GC, Tokyo, Japan	4-MET, phosphoric ester-monomer, UDMA, TEGDMA, acetone, water, stabilizer, silica filler, water, photo-initiator	2	Light cure	Dry
Hybrid Bond	Sun Medical Co, Shiga, Japan	*Hybrid base*: water, acetone, 4-META, polyfunctional acrylate, monomethacrylates, photo-initiators, stabilizer *Hybrid brushes*: sodium p-toluenesulfinate and aromatic amine adsorbed on the brush-hairs	2.5	Light cure	Dry
iBond	Heraeus Kulzer, Hanau, Germany	UDMA, 4-META, glutaraldehyde, acetone, water, photo-initiators, stabilizers	2	Light cure Contains glutaraldehyde	Dry
One-up F Bond	Tokuyama Dental Corporation, Tokyo, Japan	*Bonding Agent A*: MAC-10, photo-initiator, methacryloylalkyl acid phosphate, multi-functional methacrylic monomers *Bonding Agent B*: MMA, HEMA, water, F-deliverable micro-filler (fluoro-alumino-silicate glass), photo-initiator	Bonding agent A:0.3 Bonding agent B:8.0 Mixture:1.2	Light cure Contains special ternary catalysts to enhance coupling with chemically-cured composites Color-indicator	Dry
One-up Bond F Plus	Tokuyama Dental Corporation, Tokyo, Japan	*Bonding agent A*: MAC-10, photo-initiator, methacryloylalkyl acid phosphate, multi-functional methacrylic monomer *Bonding agent B*: MMA, HEMA, water, F-deliverable micro-filler (fluoro-alumino-silicate glass), photo-initiator	Bonding agent A:0.7 Bonding agent B:7.7 Mixture:1.2	In addition to the above features for One-up F Bond, less technical sensitivity is featured	Dry and moist
Reactmer Bond	Shofu Inc, Kyoto, Japan	*Bond A*: F-PRG filler, fluoro-alumino silicate glass, water, acetone, initiator *Bond B*: 4-AET, 4-AETA, HEMA, UDMA, photo-initiator	2.6	Fluoride releasing Light cure	Dry
Tyrian SPE	Bisco Inc, Schaumburg, IL, USA	*Primer A*: thymol blue, ethanol, water *Primer B*: AMPS, BidMEP (Bis[2-ethyl]phospate), TPO, ethanol		Color indicator Can be used as self-etching primer together with All-Bond2, One-Step and One Step Plus	Dry
Unicem	3 M ESPE, ST Paul, MN, USA	*Liquid*: methacrylated phosphoric acid ester, dimethacrylates, photo-initiator, stabilizer *Powder*: glasspowder, silica, calciumhydroxide, initiator, pigment, polymer		Dual cure	
Xeno III (Xeno CF II in japan)	DENTSPLY De Trey, Konstanz, Germany	*Bottle A*: HEMA, ethanol, water, aerosil, stabilizers (BHT)	<1		Dry

Table 1 (*continued*)

Adhesive	Manufacturer	Composition	pH	Remarks	Dry or wet bonding
	DENTSPLY Sankin Kogyo, Otahara, Japan	*Bottle B*: Pyro-EMA, PEM-F, UDMA, CQ, BHT, ethyl-4-dimethylaminobenzoate (co-intiator)			
Xeno IV	DENTSPLY Caulk, Milford, DE, USA	PENTA, Mono-, Di- and Trimethacrylate resins, cetylamine hydrofluoride, acetone–water	~2.1		Dry

Data provided by the manufacturer. The adhesives are categorized according to the classification of Van Meerbeek [5]. Abbreviations: see Table 2.

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, carboxyl 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 that 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]. DMAE-MA (Fig. 3) is a water-soluble monomer that has a tertiary amine 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 2
Abbreviations of monomers, initiators and inhibitors, filler particles and coupling factors used in adhesives

Abbreviations monomers
4-AETA: 4-acryloyloxyethyl trimellitate anhydride
4-AET: 4-acryloylethyl trimellitic acid
AMPS: 2-acrylamido-2-methyl-1-propanesulfonic acid
Bis-MEP: bis[2-(methacryloyloxy)ethyl] phospate
Bis-EMA: ethoxylated bisphenol A glycol dimethacrylate
Bis-GMA: bisphenol A diglycidyl methacrylate
BPDM: biphenyl dimethacrylate or 4,4′-dimethacryloyloxyethyloxycarbonylbiphenyl-3,3′-dicarboxylic acid
Di-HEMA phosphate: di-2-hydroxyethyl methacryl hydrogenphosphate
DMAEMA: dimethylaminoethyl methacrylate
EAEPA: ethyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate
EGDMA: ethyleneglycol dimethacrylate
GDMA: glycerol dimethacrylate
GPDM: glycerol phosphate dimethacrylate
HDDMA: 1,6-hexanediol dimethacrylate
HEMA: 2-hydroxyethyl methacrylate
HEMA-phosphate: 2-hydroxyethyl methacryl dihydrogenphosphate
HFGA-GMA: hexafluoroglutaric anhydride-glycerodimethacrylate adduct
HPMA: 2-hydroxypropyl methacrylate
MA: methacrylic acid
MAEPA: 2,4,6 trimethylphenyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate
MAC-10: 11-methacryloyloxy-1,1′-undecanedicarboxylic acid
10-MDP: 10-methacryloyloxydecyl dihydrogenphosphate
MDPB: methacryloyloxydodecylpyridinium bromide
4-META: 4-methacryloyloxyethyl trimellitate anhydride
4-MET: 4-methacryloyloxyethyl trimellitic acid
MMA: methyl methacrylate
MMEP: mono-2-methacryloyloxyethyl phthalate (sometimes also called PAMA: phtalic acid monomethacrylate)
5-NMSA (or MASA): *N*-methacryloyl-5-aminosalicylic acid
NPG-GMA: *N*-phenylglycine glycidyl methacrylate
NTG-GMA: *N*-tolylglycine glycidyl methacrylate or *N*-(2-hydroxy-3-((2-methyl-1-oxo-2-propenyl)oxy)propyl)-*N*-tolyl glycine
PEGDMA: polyethylene glycol dimethacrylate
PEM-F: pentamethacryloyloxyethylcyclohexaphosphazene monofluoride
PENTA: dipentaerythritol pentaacrylate monophosphate
Phenyl-P: 2-(methacryloyloxyethyl)phenyl hydrogenphosphate
PMDM: pyromellitic diethylmethacrylate or 2,5-dimethacryloyloxyethyloxycarbonyl-1,4-benzenedicarboxylic acid
PMGDM: pyromellitic glycerol dimethacrylate or 2,5-bis(1,3-dimethacryloyloxyprop-2-yloxycarbonyl)benzene-1,4-dicarboxylic acid
Pyro-EMA: tetramethacryloyloxyethyl pyrophosphate
TCB: butan-1,2,3,4-tetracarboxylic acid di-2-hydroxyethylmethacrylate ester
TEGDMA: triethylene glycol dimethacrylate
TMPTMA: trimethylolpropane trimethacrylate
UDMA: urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,3′,5-trimethylhexaan

Abbreviations initiators and inhibitors
BHT: butylhydroxytoluene or butylated hydroxytoluene or ,2,6-di-(tert-butyl)-4-methylphenol (inhibitor)
BPO: benzoylperoxide (redox initiator)
BS acid: benzenesulfinic acid sodium salt (redox initiator)
CQ: camphorquinone or camphoroquinone or 1.7.7-trimethylbicyclo-[2,2,1]-hepta-2,3-dione (photo-initiator)
DHEPT: *N*,*N*-di-(2-hydroxyethyl)-4-toluidine (co-initiator)
MEHQ: 4-methoxyphenol or monoethyl ether hydroquinone (inhibitor)
ODMAB: 2-(ethylhexyl)-4-(dimethylamino)benzoate (co-initiator)
TPO: Lucirin TPO, BASF (photo-initiator)
UV-9: 2-hydroxy-4-methoxybenzophenone (photo-initiator)

Abbreviations fillers and silane coupling factors
Coupling factor A174: γ-methacryloxypropyltrimethoxysilane
F-PRG: full reaction type pre-reacted glass-ionomer fillers
NaF: sodium fluoride
Na_2SiF_6: disodium hexafluorosilicate
POSS nano-particulates: polyhedral oligomer silsesquioxanes

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

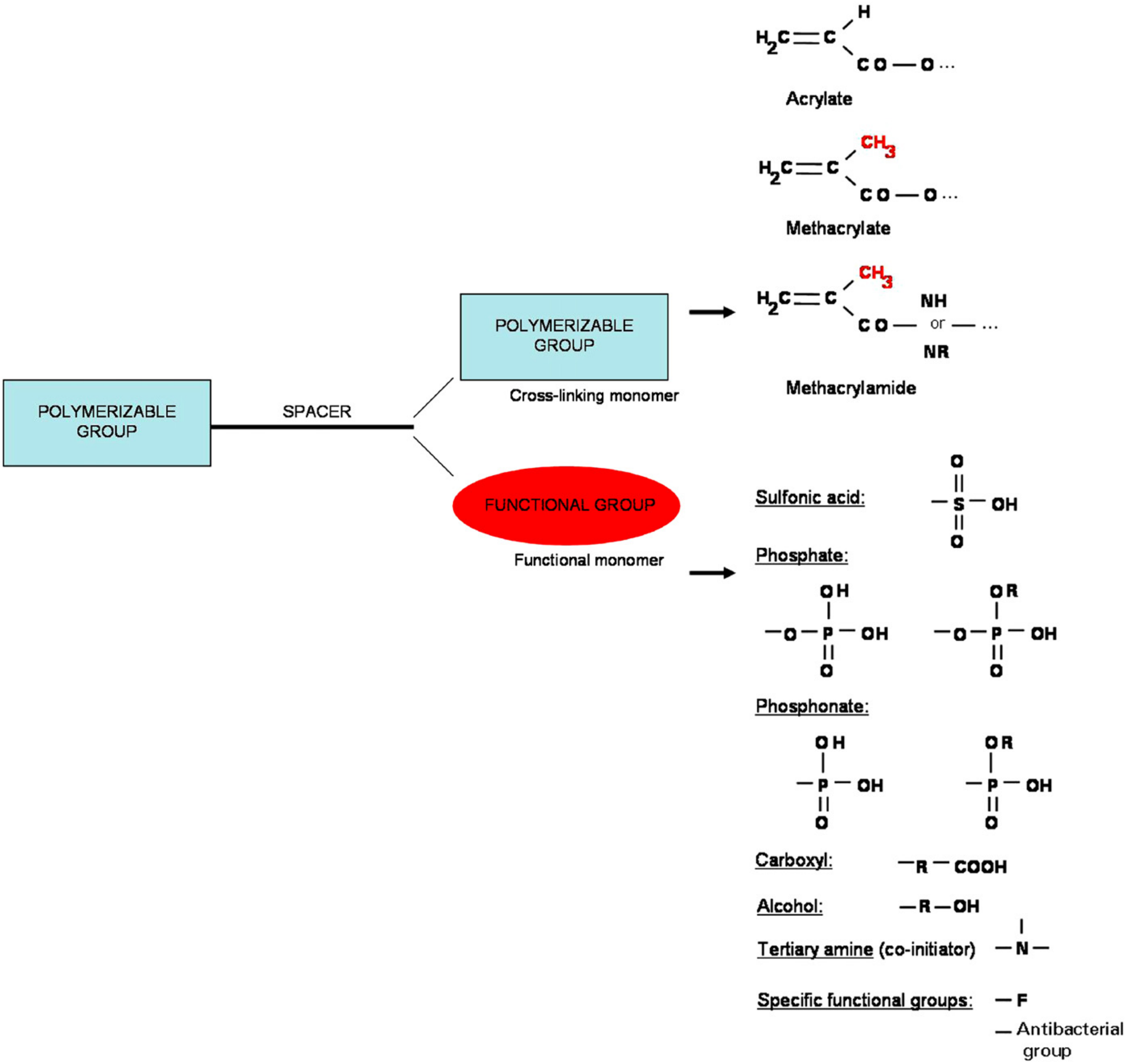


Fig. 2. General make-up of either a cross-linking or a functional monomer. The vast majority of monomers currently used in adhesives correspond to this structure. Moreover, adhesive monomers belong usually to the group of methacrylates.

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 ormocer (organically modified ceramics). These polymers have a polymerized backbone of SiO_2 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].

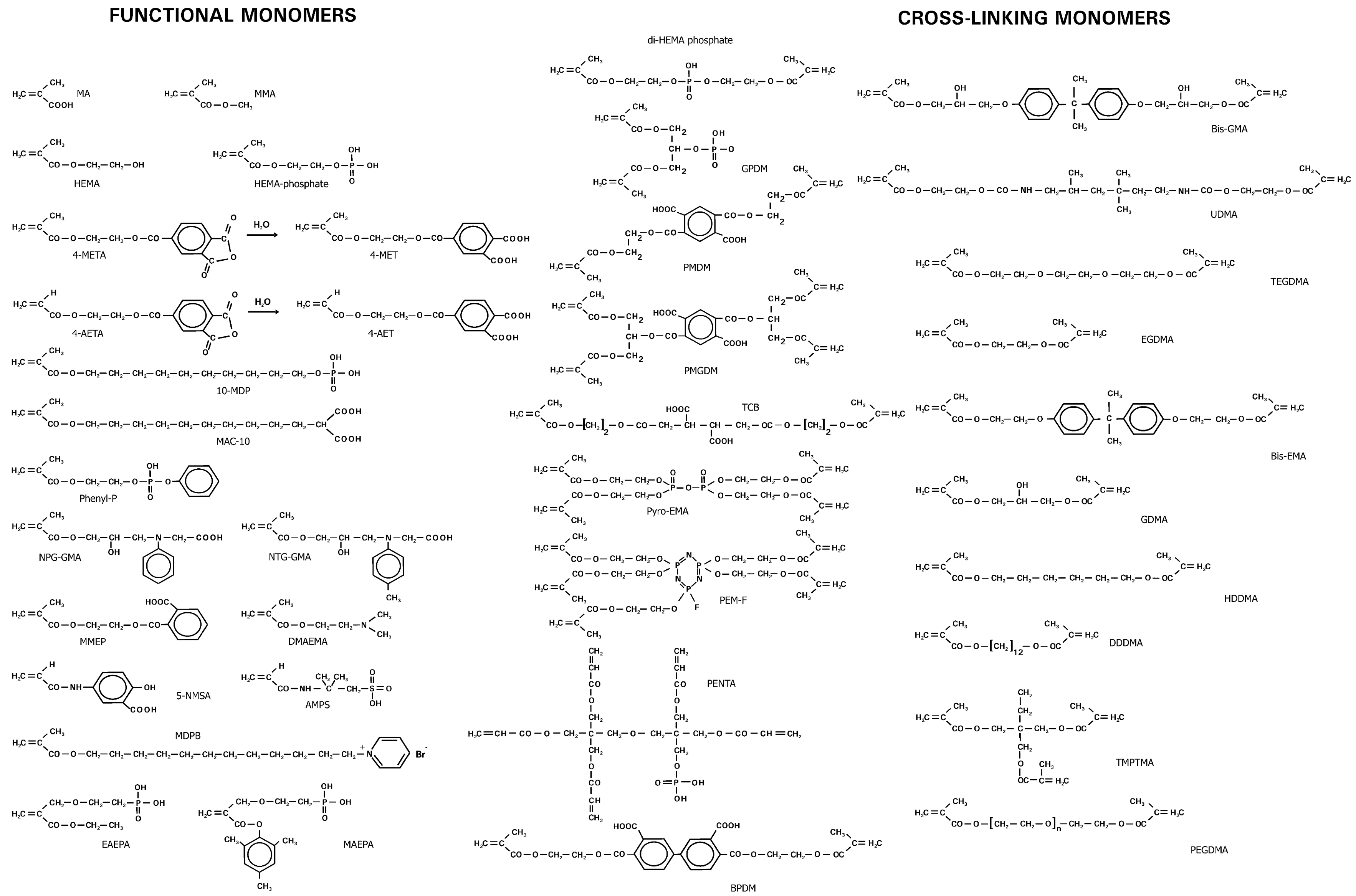


Fig. 3. Chemical structure of monomers used in contemporary adhesive systems. Left are typical functional monomers, and on the right, cross-linking monomers are shown. In the center, some monomers with several polymerizable groups are shown, that also exhibit at least one functional group. Some of them however will dissociate in aqueous solutions to form monomers with one polymerizable group. Abbreviations: see Table 2.

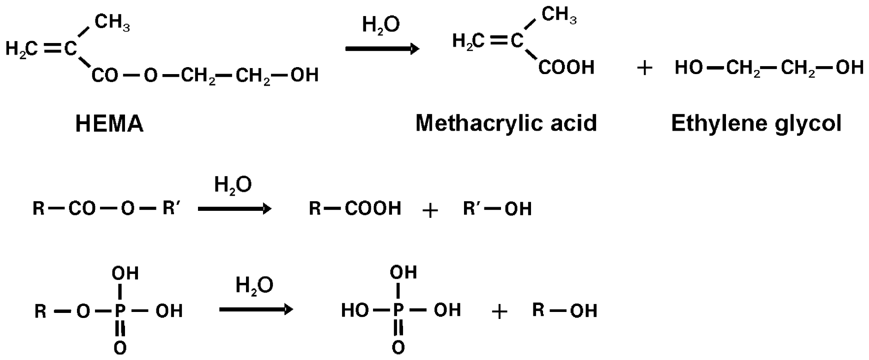


Fig. 4. Some chemical groups are susceptible to hydrolysis, especially in acidic environment. The ester group, typical of all methacrylate monomers, is vulnerable to hydrolytic dissociation. Here, hydrolysis of HEMA is shown, resulting in MA and ethylene glycol. Likewise, other ester groups in a monomer can also be hydrolyzed, to form a carboxylic acid. Unlike phosphonate groups, phosphate groups are also at risk of hydrolysis, resulting in release of phosphoric acid into the adhesive. Both last described reactions may render an adhesive more acidic with increased shelf time.

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 deducted 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

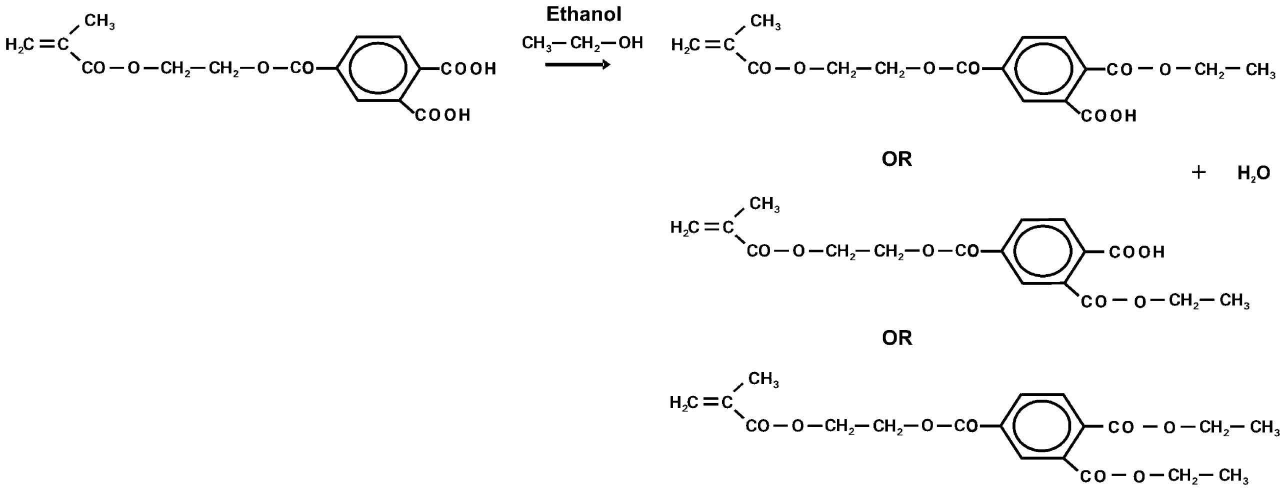


Fig. 5. Esterification of 4-MET when mixed with ethanol as solvent. One of the carboxylic groups may react in an esterification reaction with subsequent inactivation of the carboxylic group for demineralization and adhesion promotion. A negligible amount of di-ethyl ester of 4-MET will also be formed.

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 groups with the hydroxyl group can occur, especially in acidic conditions (Fig. 5) [68]. Many authors have reported improved adhesion to enamel and dentin due to the addition of 4-MET [74]. 4-MET is also frequently used together with MMA in the so-called 4-META/MMA TBB adhesive [57,58,75]. Recently, Yoshida et al. [7] showed that 4-MET is able to establish an ionic bond with calcium in hydroxyapatite, though, less intense than other functional monomers, such as 10-MDP (see below). Moreover, the resulting Ca-4MET salt has a relatively high solubility and is therefore not very stable.

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 (Fig. 3) [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

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-phospate 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 mono-methacrylates 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

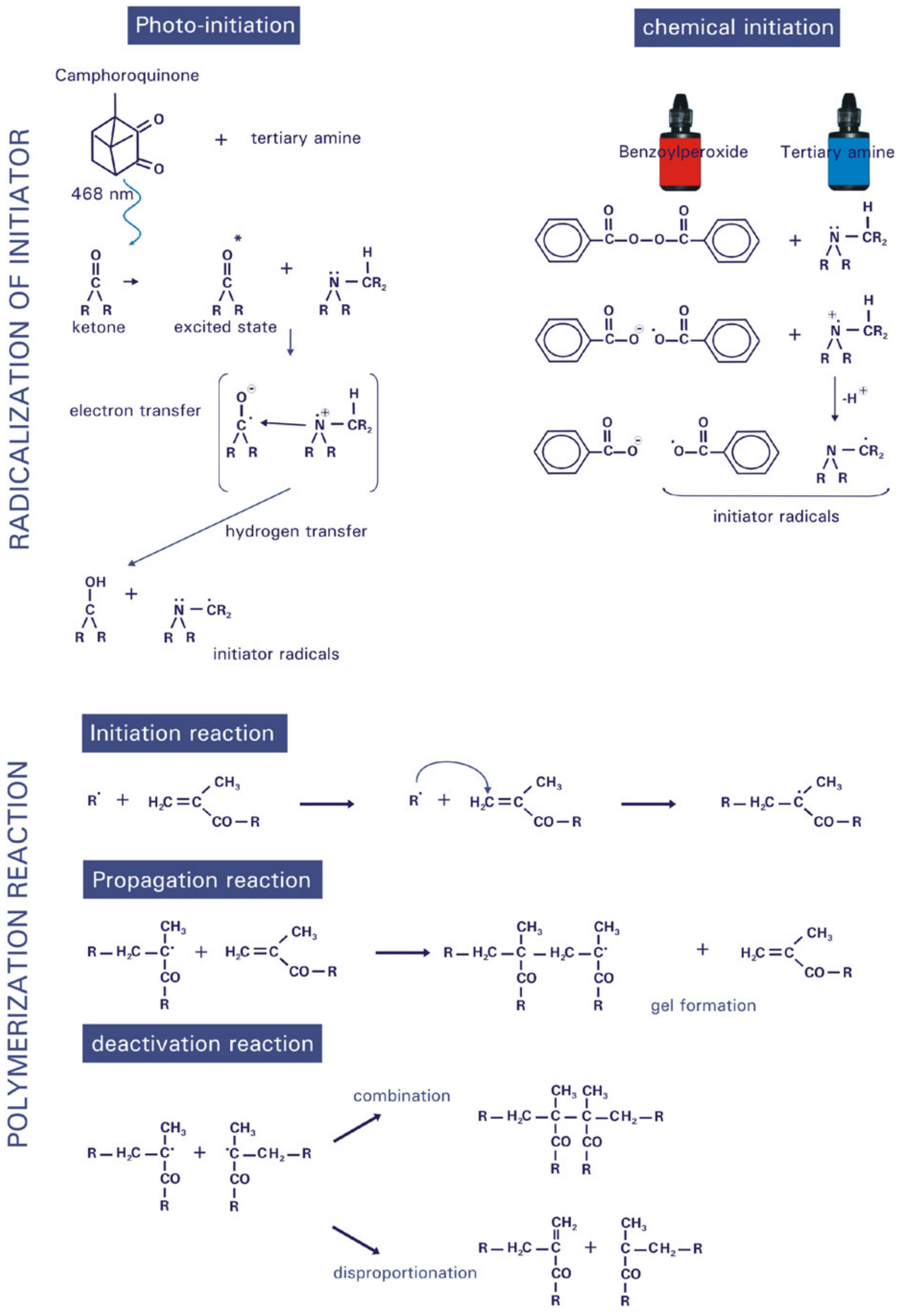


Fig. 6. (Meth)acrylates and (meth)acrylamides in adhesives polymerize due to a radical polymerization reaction. At the top of the figure, the radicalization reaction of two main initiators in dental adhesives is shown. Camphorquinone is a typical photo-initiator, while benzoylperoxide is a thermal initiator 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 hydrogentransfer and formation of two dead polymer chains (one saturated and one unsaturated) [113,114].

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

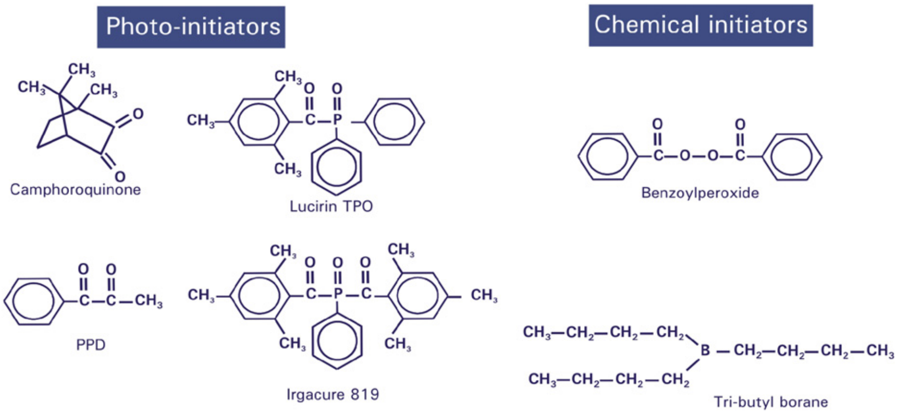


Fig. 7. Chemical structure of photo-initiators and chemical initiators used in commercial adhesive systems. Typical are the aromatic rings in photo-initiators, which will provided absorption of electromagnetic waves.

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) diphenylphoshine oxide or TPO (Lucirin TPO, BASF), a monoacylphosphine (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 Irguracure is best light cured by a high-power LED device. Due to the three-phenyl groups, TPO and also Irguracure are rather hydrophobic molecules that are difficultly dissolvable in water [136]. These photo-initators 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 standardly 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 benzoylperoxide (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 photo-initiators (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 anti-oxidants 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.

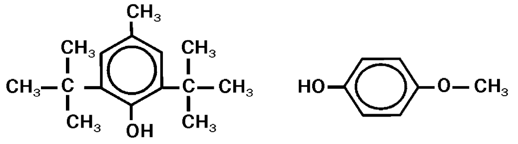

BHT MEHQ

Fig. 8. Chemical structure of the two most frequently used inhibitors in adhesive systems. Abbreviations: BHT: butylated hydroxytoluene; MEHQ: monomethyl ether hydroquinone.

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.

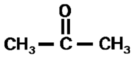
Most important characteristics of a solvent are its dipole moment, dielectric constant, boiling point, vapor pressure and H-bonding capacity (Table 3). The vapor pressure of a solvent is important to ensure good evaporation of the solvent after application of the adhesive onto tooth tissue [148,149]. 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 3
Main characteristics of solvents used in adhesives

	Dipole moment in gaseous state in Debye at 25 °C	Dielectric constant at 293°K (20 °C)	Boiling temperature (°C)	Vapor pressure in mmHg at 25 °C	H-bonding capacity
Water H_2O	1.85	80	100.0	23.8	+ + +
Ethanol $CH_3–CH_2–OH$	1.69	24.3	78.5	54.1	+
Acetone  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	2.88	20.7	56.2	200	–

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 volatity 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

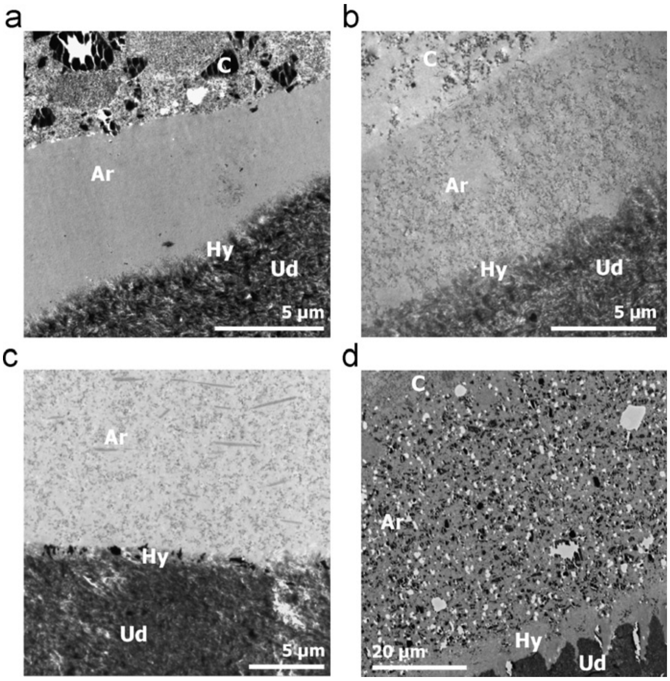


Fig. 9. Transmission electron photomicrographs showing the adhesive layer of several adhesives bonded to dentin. (a) TEM of iBond (Heraeus-Kulzer), an unfilled 1-SEA. No filler particles can be found in the adhesive layer. (b) TEM of G-Bond (GC), a 1-SEA filled with nano-sized silica particles. Filled 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.

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 may be loaded up to 50 wt% [168]. Second, the size of the filler particles is a key factor enabling the filled resin to penetrate into dentin tubules and possibly also the collagen network. After etching, the interfibrillar spaces of the demineralized collagen network have been shown to be in the range of 20 nm. Any appropriate size for the filler is therefore preferably less than 20 nm. Consequently, nanometer-sized silica (pure silicon dioxide), from either colloidal or pyrogenic origin are most frequently added, which also implies that only small concentrations of filler can be added due to their unfavorable surface area to weight ratio [22]. Nevertheless, in spite of their small size (up to 7 nm and smaller), debate still exists as to whether these particles can actually infiltrate demineralized collagen networks. Moreover, it has been reported that exposed collagen may even function as a filter [171,192].

Regarding the filler composition, they run the gamut from silicon dioxide to composed silicate glasses containing heavy metal atoms such as barium and strontium, tailored to provide radio-opacity to the resin. However, most filled adhesive resins for bonding composites contain only pure silicon dioxide (either colloidal silica or pyrogenic silica), and are consequently not radio-opaque. In addition, adhesive systems are generally not filled to a level, which will yield clinically effective radio-opacity. Fluorine-containing reactive silicate glasses are sometimes added with the intention to release fluoride (Imperva Fluorobond, Shofu; One-up F Bond, Tokuyama; Optibond adhesives, Kerr). Reactmer Bond (Shofu) contains both conventional fluoro-alumino-silicate glasses and pre-reacted glass polyalkenoate fillers as a source of fluoride. It is assumed that the acidic monomers function in water as donors of protons, which can react with the fluoro-alumino silicate glass (proton acceptor) following a typical glass-ionomer acid–base reaction. Subsequently, a chemical bond between the fluoro-alumino-silicate glass and the resin may be formed and fluoride released. Clearfil Protect Bond (Kuraray) contains polysiloxane-encapsulated sodium fluoride particles, serving the same purpose (Fig. 9). The clinical benefit of fluoride release from bonding systems and its effect on the recurrence of caries, however, still need to be established [172]. A particular type of nano-sized filler is used in Nano-Bond (Pentron) (Table 1). This 2-SEA contains POSS particles (polyhedral oligomeric silsesquioxane), which have a unique cage structure (–Si–O) that can be covalently bonded on the outside with functional groups, such as methacrylate groups [173].

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 $(-\mathrm{Si}-(\mathrm{CH}_3)_2-)$ and trimethylsilyl $(-\mathrm{Si}-(\mathrm{CH}_3)_3)$ 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 polyalkenoic 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 pretreating 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], allergenic [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.

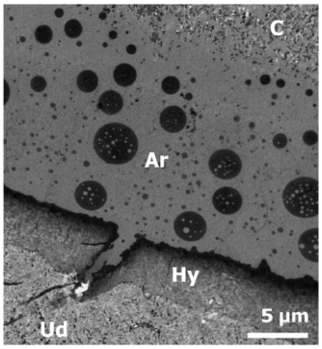


Fig. 10. Transmission electron photomicrograph of Adper Scotchbond XT1 (Scotchbond 1 XT) on dentin. TEM-section stained with uranyl acetate and led citrate. Notice how the poly-alkenoic co-polymer forms a different phase in the adhesive layer, resulting in multiple globules with varying size.

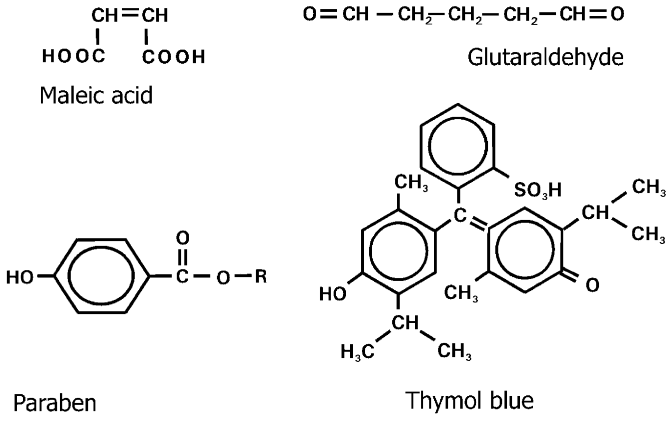


Fig. 11. Manufacturers sometimes add specific ingredients. The chemical structure of some of these ingredients is shown in this figure.

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 parabenes (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, $C_{16}H_{35}NHF$), 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 homogenous 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).

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 unwise. Lining with $Ca(OH)_2$ is still very much advocated.

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.

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