50 Acrylic Resins

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Core Messages

- Contact allergy to acrylic resin monomers is most often induced by dental products, artificial nails, and anaerobic glues, which usually contain aliphatic methacrylates. Patients exposed to methacrylate products commonly have allergic reactions to a large number of different methacrylates. 2-Hydroxyethyl methacrylate (2-HEMA), ethyleneglycol dimethacrylate (EGDMA), and 2-hydroxypropyl methacrylate (2-HPMA) are the most commonly positive, due to the strong cross-allergy between them. Other commonly positive methacrylates include ethyl methacrylate (EMA), methyl methacrylate (MMA), triethyleneglycol dimethacrylate (TREGDMA), and tetrahydrofurfuryl methacrylate (THFMA). Patients have not necessarily been exposed to all patch-test-positive methacrylates.
- Some products contain mostly aliphatic acrylates, e.g., UV-cured printing inks, lacquers, paints, varnishes, and glues. Contact allergy to acrylates is relatively rare. The main aliphatic acrylate allergens in these products include tripropyleneglycol diacrylate (TPGDA) and dipropyleneglycol diacrylate (DPGDA). Exposure to acrylates does usually not lead to cross-allergy to methacrylates.
- Dental composite resins, UV-curable printing inks, and some glues contain epoxy acrylates such as bis-GMA and bis-GA. Most of the reactions to epoxy acrylates are cross-allergies to epoxy resin – about 20% of epoxy resin allergic patients react to some epoxy acrylates. Specific allergy to epoxy acrylates is rare, and diagnosis requires testing with the specific compound(s).
- Cyanoacrylates and acrylamide derivatives are also rare independent allergens, which cannot be screened by other acrylic compounds, e.g., 2-HEMA.
- Allergic contact dermatitis from acrylic resins typically affects the fingertips.
- Risk occupations include dentists, dental nurses, dental technicians, nail technicians, assemblers of machines and mechanical devices, printers, painters, and workers in paint factories.

1 Introduction

Acrylic resins are a group of plastic substances derived from acrylic acid, methacrylic acid, and other related compounds. Acrylic acid is a carboxylic acid with a carbon-carbon double bond connected to its acid functionality (➲ *Fig. 50.1*). The carbon-carbon double bond (a vinyl group) is the reactive group responsible for the formation of plastics by polymerization. The monomers include acrylic acid and methacrylic acid and their esters, cyanoacrylic acid and its esters, acrylamides, and acrylonitrile. A large number of different acrylic polymers are formed from the monomers, and can be combined with other types of resins such as epoxies, polyurethanes, polyesters, and polyethers.

2 Chemical Structures and Main Uses

2.1 Acrylic Acid and its Esters (Acrylates)

Acrylic acid and its esters, which are also known as acrylates (➲ *Fig. 50.1*), are flammable, volatile, colorless liquids. They all polymerize very easily. Polymerization is catalyzed by heat, light, and peroxides, and inhibited by stabilizers such as the monomethyl ether of hydroquinone, or hydroquinone itself. These phenolic inhibitors are only effective in the presence of oxygen (Ohara et al. 2010).

The primary role of acrylic acid in the production of acrylates is as an intermediate. Acrylic esters are used exclusively for the production of polymers (polyacrylates). Polymers are used mainly in coatings, paints, adhesives, binders for leather, paper, and textiles. About 80% of the methyl acrylate (MA) produced is used as a copolymer component of acrylic fibers. Ethyl acrylate (EA) is used for both solvent- and water-based paints, and in textiles as a binder in nonwoven fabrics and flocking. Butyl acrylate (BA) is mainly used in water-based paints and adhesives. 2-Ethylhexyl acrylate (2-EHA) is used for almost the same purposes as butyl acrylate, in stick-on labels, and in the caulking of building materials. The above mentioned

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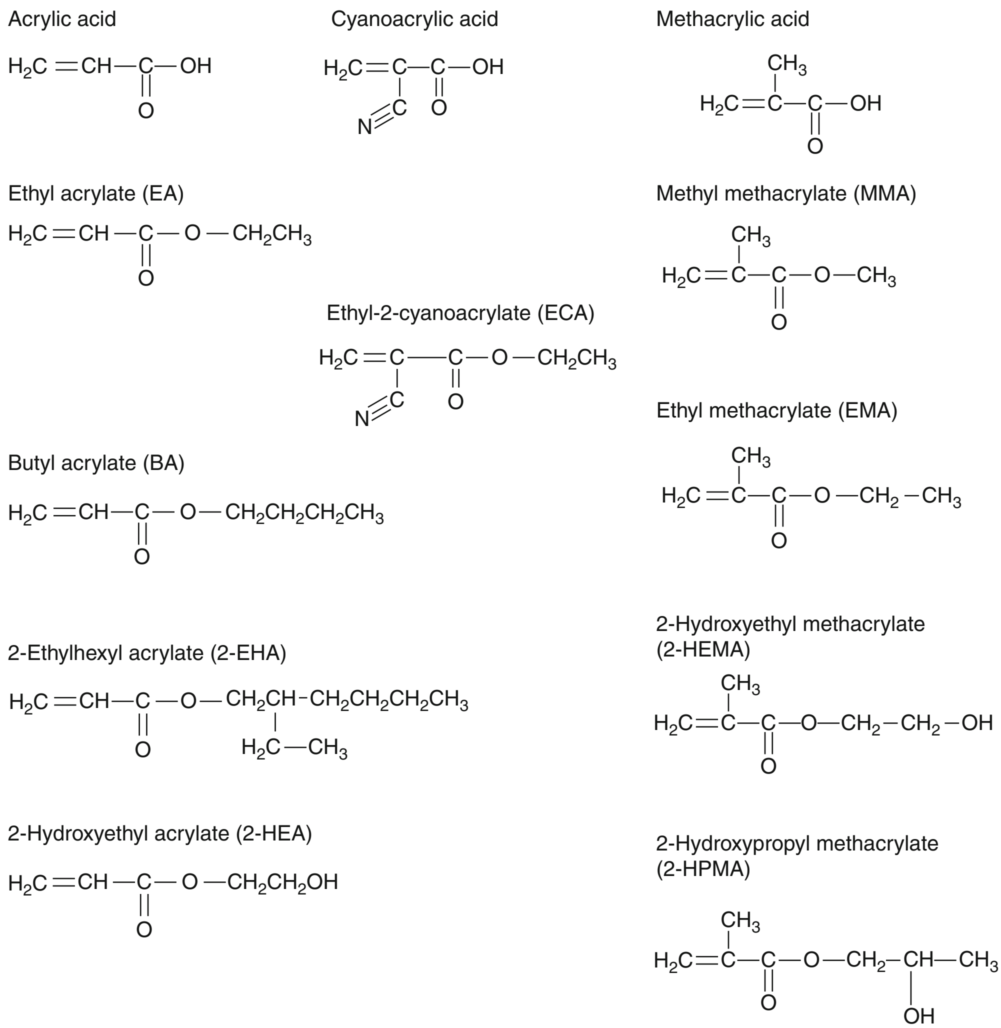


Fig. 50.1
Acrylic acid, cyanoacrylic acid, methacrylic acid, and their monoesters

acrylates have only one reactive acrylic group and are called monoacrylates (Fig. 50.1). Compounds with at least two reactive groups are called multifunctional acrylates. Representative multifunctional acrylates comprise trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate (PETA), 1,4-butanediol diacrylate (1,4-BUDA), 1,6-hexanediol diacrylate (1,6-HDDA), and poly(ethylene glycol) diacrylates (Figs. 50.2, 50.3, 50.4). These esters of polyhydric alcohols are used as cross-linking agents and modifiers in rubber and synthetic resins, in adhesives, and as active diluents in photosensitive resins. They are also applied in the coating and ink industries because they can be cured with ultraviolet light or electron-beam radiation. Examples of two industrially significant esters are 2-hydroxyethyl acrylate (2-HEA) and 2-hydroxypropyl acrylate (2-HPA), which are particularly used as cross-linking agents in heat-cured paints, adhesives, and textile preparations, etc. (Fig. 50.1) (Ohara et al. 2010) (Table 50.1).

2.2 Methacrylic Acid and its Esters (Methacrylates)

Methacrylates are esters of methacrylic acid, which has an additional methyl group compared to acrylic acid (Fig. 50.1). Compounds with one methacrylic group are called monomethacrylates (Fig. 50.1), and those

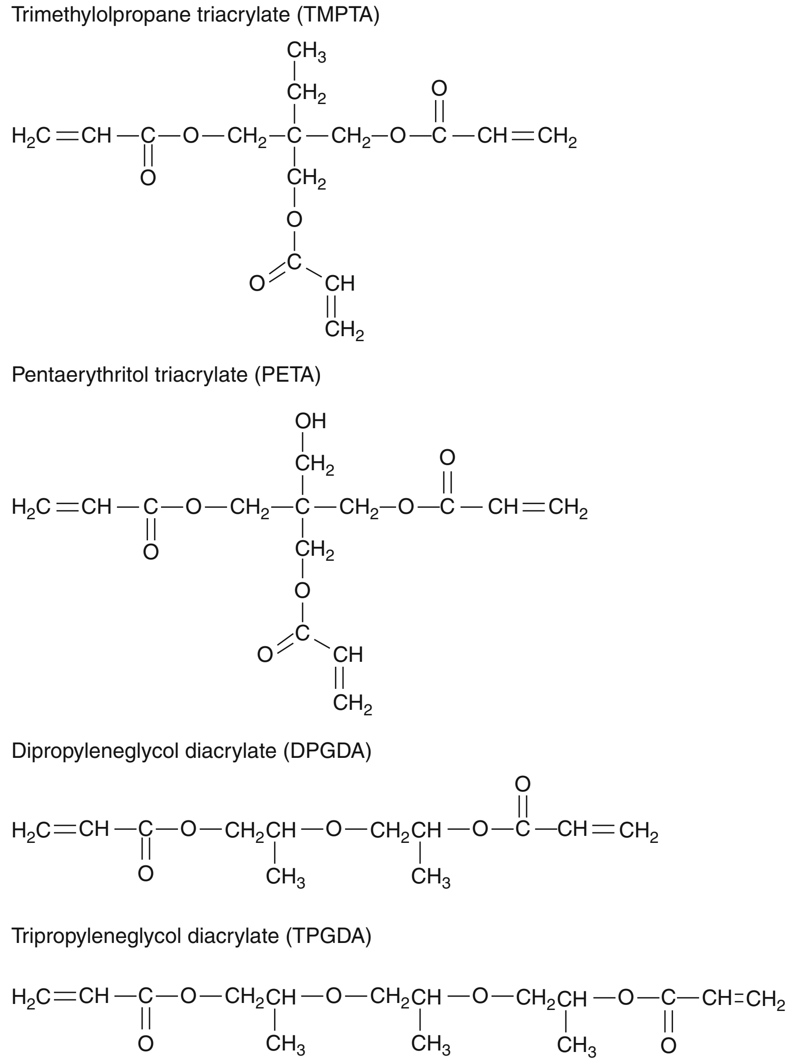


Fig. 50.2
Some multifunctional acrylates

with at least two methacrylic groups are called multifunctional methacrylates (*Figs. 50.3*, *50.4*). Methacrylic acid and methacrylate esters are used to prepare a wide range of polymers. Polymethyl methacrylate (PMMA) is the primary polymer in this category, and provides water-clear, tough plastics that are used in sheet form in glazing, signs, displays, and lighting panels. Automotive lighting lenses and similar products can be prepared from molding pellets. Methyl methacrylate, incorporated into copolymers, forms the basis for durable coatings and inks. Higher methacrylate polymers are useful in the manufacture of oil additives, solvent-free inks and coatings, and binders for xerography. Salts of polymethacrylic acid can serve as the basis for water-soluble thickeners and detergent additives (Bauer 2010). As regards contact allergy, important applications include dental restorative materials, dentures, artificial nails, glues, and orthopedic cements.

2.3 Cyanoacrylates

Cyanoacrylates are based on cyanoacrylic acid (*Fig. 50.1*). 2-cyanoacrylates are utilized almost exclusively as instant adhesives. Methyl, ethyl, butyl, allyl, and methoxyethyl 2-cyanoacrylates are available for a wide

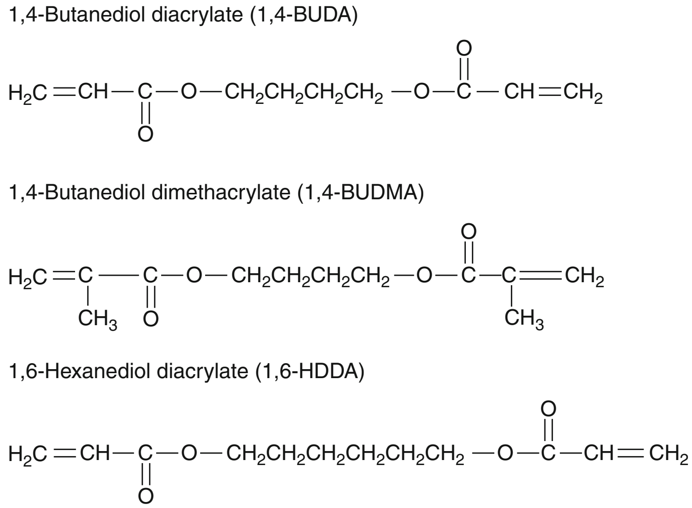


Fig. 50.3
Some multifunctional (meth)acrylates

field of applications. They are used in the electrical and electronics industries, as well as in many areas of mechanical engineering such as automobile, ship, and aircraft construction. In addition to these purely technical applications, 2-cyanoacrylates are used in medicine to close wounds, and in artificial nail glues (Ohara et al. 2010).

2.4 Epoxy Acrylates (Acrylated Epoxy Resins)

Epoxy resins are reacted with acrylic acid to form epoxy acrylates (*Fig. 50.5*), which can be cured by light (most commonly UV lights) or electron beams. Epoxy diacrylate, named also bis-GA, 2,2-Bis[4-(2-hydroxy-3-acryloxypropoxy)phenyl]-propane or epoxy acrylate, is the diacrylate of the diglycidyl ether of bisphenol A (DGEBA) epoxy resin. Major applications include coatings for overprint varnishes, wood substrates, and plastics. Both aromatic and aliphatic epoxy acrylates exist, as well as acrylated epoxidized oils such as soybean oil and linseed oil (Bjorkner 2006; Pham and Marks 2010). In the 1960s, the first epoxy methacrylate, 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (bis-GMA; also named bisphenol A diglycidyl-methacrylate or epoxy dimethacrylate), was developed for dental composite resins. It is manufactured by reacting DGEBA with methacrylic acid, or bisphenol A with glycidyl methacrylate (Jolanki et al. 2000b). 2,2-Bis[4-(methacryl-oxyethoxy)phenyl] propane (bis-EMA) and 2,2-bis[4-(methacryloxy)phenyl]-propane (bis-MA) have been developed as substitutes for bis-GMA.

2.5 Combinations with Other Plastics

Acrylic resins can be combined with other resins to form, e.g., urethane acrylates, polyester acrylates, polyether acrylates. These compounds are used as prepolymers in dental composites, UV-curable inks, varnishes, and coatings.

2.6 Acrylamide and Derivatives

Acrylamide is used to produce water-soluble polymers or copolymers used for paper manufacturing, waste treatment, mining applications, and enhanced oil recovery (Langvardt 2010). Acrylamide and its derivatives are also used in the production of photopolymer printing plates and polyacrylamide electrophoresis.

2.7 Acrylonitrile

Acrylic textile fibers are by far the largest end-use product for acrylonitrile, which is also used for nitrile rubber and in the production of acrylonitrile-butadiene-styrene and styrene-acrylonitrile resins. These products are used to

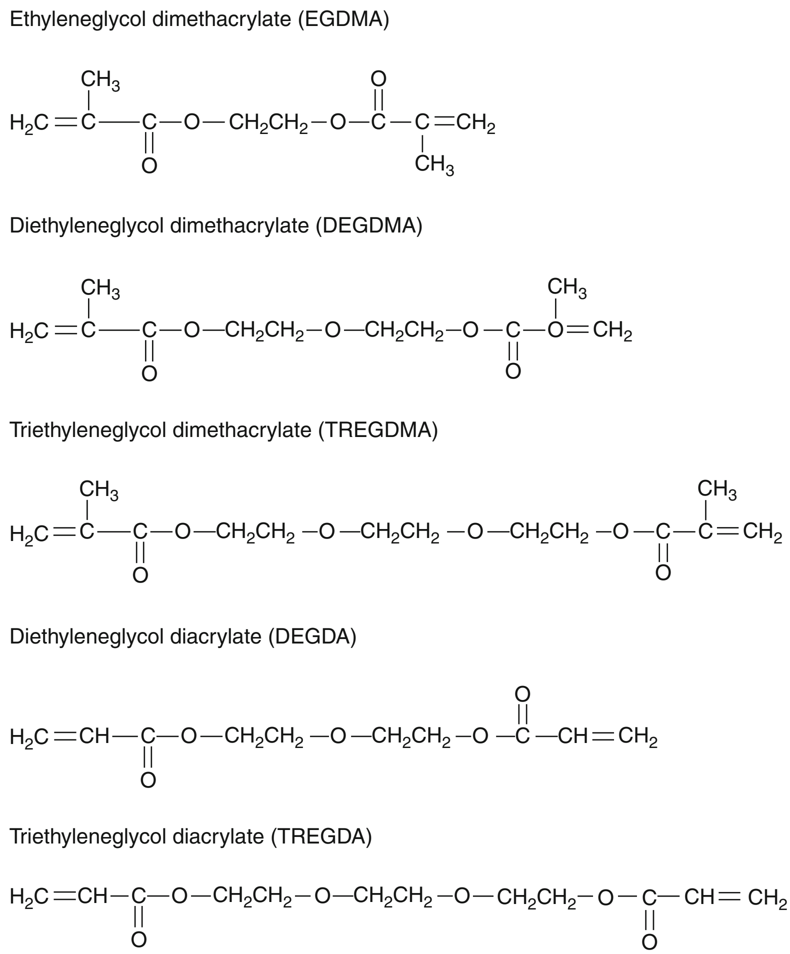


Fig. 50.4
(Poly)ethylene glycol di(meth)acrylates

fabricate components for automotive and recreational vehicles, pipe fittings, house ware, electrical appliances, suitcases, and disposable dishes (Bjorkner 2006; Langvardt 2010).

2.8 Radiation Curing Systems

Radiation curing is a relatively new technology which uses electromagnetic (mainly UV) or ionizing (mainly accelerated electrons) radiation to initiate a chain reaction in which mixtures of polyfunctional compounds are transformed into a cross-linked polymer network. During irradiation with UV light, the reactive species are formed by the chemical decomposition of a photo initiator. Radiation-cured systems can be based on several resin systems. Prepolymers and monomers bearing acrylic functionalities dominate the market. Products with methacrylic groups have special end uses, e.g., in dental products and in the electronics industry. Other resin systems include polyester-styrene mixtures, thiol-thiene mixtures, and epoxy resins (Streitberger et al. 2010).

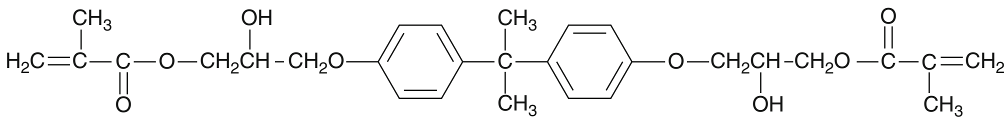
A UV-curable acrylate system usually contains four main components: prepolymer(s), monomer(s), photo initiator(s), and additives. The most common prepolymers are acrylated epoxy resins. In acrylated urethanes, an isocyanate-functional prepolymer with a polyol backbone can be reacted with a hydroxy-functional monomer (e.g., 2-HEA or 2-HPA). Polyester acrylates are another example of commercially significant prepolymers; they are used in a wide range of applications from

Table 50.1 Abbreviations

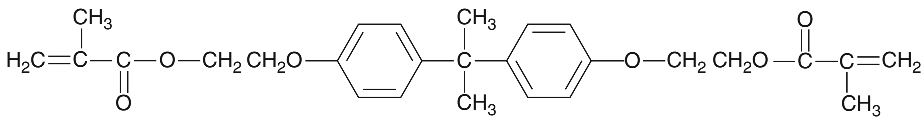
Acrylic monomer	Abbreviation
Acrylates	
Methyl acrylate	MA
Ethyl acrylate	EA
Butyl acrylate	BA
2-Ethylhexyl acrylate	2-EHA
2-Hydroxyethyl acrylate	2-HEA
2-Hydroxypropyl acrylate	2-HPA
1,4-Butanediol diacrylate	BUDA
1,6-Hexanediol diacrylate	HDDA
Diethyleneglycol diacrylate	DEGDA
Triethyleneglycol diacrylate	TREGDA
Pentaerythritol triacrylate	PETA
Dipropyleneglycol diacrylate	DPGDA
Tripropyleneglycol diacrylate	TPGDA
Trimethylolpropane triacrylate	TMPTA
Isobornyl acrylate	IBA
Oligotriacrylate 480	OTA480
Urethane diacrylate, aliphatic	al-UDA
Urethane diacrylate, aromatic	ar-UDA
Methacrylates	
Methyl methacrylate	MMA
Ethyl methacrylate	EMA
N-Butyl methacrylate	BMA
2-Hydroxyethyl methacrylate	2-HEMA
2-Hydroxypropyl methacrylate	2-HPMA
Ethyleneglycol dimethacrylate	EGDMA
Diethyleneglycol dimethacrylate	DEGDMA
Triethyleneglycol dimethacrylate	TREGDMA
Tetraethyleneglycol dimethacrylate	TETEGDMA
Pentaethyleneglycol dimethacrylate	PEGDMA
Tetrahydrofurfuryl methacrylate	THFMA
1,4-Butanediol dimethacrylate	BUDMA
N,N-Dimethylaminoethyl methacrylate	DMAEMA
Urethane dimethacrylate	UDMA
Polymethyl methacrylate	PMMA
Others	
Ethyl cyanoacrylate	ECA
N,N-Methylenebisacrylamide	MBAA
Epoxy (meth)acrylates	
Epoxy diacrylate (epoxy acrylate)	bis-GA
2,2-bis[4-(2-Hydroxy-3-methacryl-oxypropoxy)phenyl] propane	bis-GMA
2,2-bis[4-(Methacryl-oxyethoxy) phenyl] propane	bis-EMA
2,2-bis[4-(Methacryloxy) phenyl]propane	bis-MA
Glycidyl methacrylate	GMA
Diglycidyl ether of bisphenol A (epoxy resin)	*DGEBA*

overprinting varnishes to lithographic (offset) inks. In radiation-curable systems, the solvent is replaced by reactive diluents (monomers) which are incorporated into the network during cross-linking. These monomers have two important functions: they reduce the viscosity of the mixture, and they strongly influence the physical and chemical properties of the final coating. Monomers can be divided into three groups: (1) Monofunctional monomers: e.g., isobornyl acrylate (IBA), N-vinylpyrrolidone, (2) difunctional monomers: e.g., 1,6-HDDA, tripropylene glycol diacrylate (TPGDA), and (3) tri- or tetrafunctional monomers: e.g., TMPTA, PETA, and pentaerythritol tetraacrylate (which increase the cross-linking density of the final coating). Compounds such as benzophenone, thioxanthone, and benzoin ethers are used as photo initiators. Additives include, e.g., pigments, fillers, defoamers and wetting agents, flatting agents, surfactants, and slip aids (Streitberger et al. 2010).

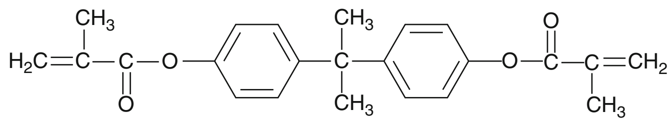
Radiation curing is used for protective coatings, inks, adhesives, and in other minor areas. Coatings for paper include clear-coats for laminated paper on pressboard (wood-grain papers to simulate natural wood). Inks and overprint varnishes for the graphic art industry, high-gloss overprint varnishes for magazine covers, record jackets, and various other consumer items are also often radiation-cured, as are plastic coatings for interior and exterior applications. The coating of wood is another important use of radiation curing, and UV-curable coatings are also used for cork in Spain and Portugal. Industrial metal applications also exist: electronics applications, photoresists, solder masks, potting compounds, and conformal coatings are all products based on UV-curable materials. Optical fibers are coated with a protective layer of UV-curable materials. Radiation-curable inks are applied to metal, paper, wood, and plastics. Lithographic (offset) and screen printing inks are the main printing inks, but flexographic inks, intaglio inks, and ink-jet printing are also used. In the printing industry, flexographic printing plates are manufactured from UV-curable materials. UV-cured adhesives on the other hand are often used in lamination,



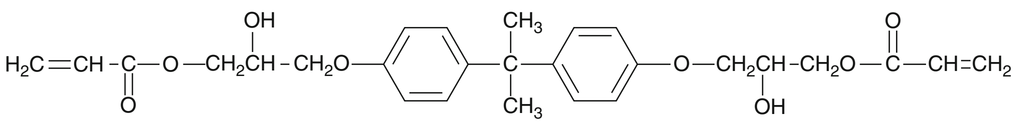
Bis-GMA



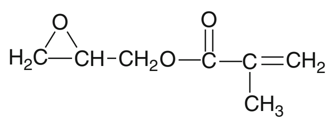
Bis-EMA



Bis-MA



Epoxy diacrylate (Bis-GA)



Glycidyl methacrylate

Fig. 50.5
Epoxy (meth)acrylates

and some UV-curable pressure-sensitive adhesives are used in the automotive industry.

An interesting application is three-dimensional modeling (stereo lithography), in which a solid part is made from a vat of UV-curable liquor by the use of UV lasers controlled by computers using CAD/CAM software. Release coatings (casting paper, caul sheet, labels) are manufactured by electron beam curing. Other new applications of radiation curing include binders for magnetic media, leather coatings, and paper upgrading (Streitberger et al. 2010).

3 Allergic Contact Dermatitis from Acrylic Resins

The cured end products of acrylic resin systems do not normally sensitize or cause symptoms in previously sensitized individuals, as they do not contain enough reactive monomers, which represent the actual contact allergens.

Uncured products, in turn, contain sensitizing monomers. Contact allergy to acrylic resin monomers is most often induced by dental products, artificial nails, and glues (Guerra et al. 1993; Tucker and Beck 1999; Geukens and Goossens 2001; Sood and Taylor 2003; Goon et al. 2006; Teik-Jin Goon et al. 2007; Aalto-Korte et al. 2008). These products usually contain methacrylates, to which patients have allergic reactions more commonly than to acrylates. 2-Hydroxyethyl methacrylate (2-HEMA), ethyleneglycol dimethacrylate (EGDMA), and 2-hydroxypropyl methacrylate (2-HPMA) are the most commonly positive allergens. Some products contain mainly acrylates, e.g., UV-cured printing inks and lacquers (Emmett 1977), paints and varnishes (Conde-Salazar et al. 2007), and glues (Fregert 1978; Whittington 1981; Kiec-Swierczynska et al. 2005). In many occupations, dermatitis typically affects the fingertips; sometimes also the hands, the forearms, and the face.

3.1 Dental Acrylates

Dental fillings are now often composed of resin-based composites, various glass-ionomers and combinations of composite resins and glass-ionomers. These essentially consist of an organic methacrylate functional resin matrix, inorganic fillers, and coupling agents. Light-curing systems are popular (Onusseit et al. 2010a). The key chemical in dental restorative resins is bis-GMA (epoxy dimethacrylate). Today, monomer mixtures of bis-GMA and triethylene glycol dimethacrylate (TREGDMA), some other dimethacrylates which act as diluents, and certain urethane dimethacrylates are used. The resins are used together with inorganic filler, usually silica, to form the composite resins. The inorganic filler material is treated with special silanes, e.g., 3-methacryloxypropyltrimethoxysilane, in order to enable a chemical bond between matrix and filler. In a more recent development, glass particles (barium or strontium silicate glass) are mixed with silica. The composites were formerly used as two-paste systems: base paste and catalyst paste. Today, light-cured one-component polymers are more common. They contain a photo initiator system: to cure the composites, visible light is used with camphoroquinone as the initiator, and aliphatic and aromatic amines as polymerization promoters, and only common halogen lamps or blue LED lights are required (Craig et al. 2006). In ormocer-based filling material, the main component of the monomer matrix is an organically modified ceramic. This is a cross-linked silicone oligomer bearing methacrylate groups. Dimethacrylates are used as diluents (Craig et al. 2006).

Carious lesions can potentially arise in the fissures of the posterior teeth. However, when these fissures are sealed with thin layers of bis-GMA or related compounds, the occlusal surfaces can largely be protected from caries. The sealant resins, such as restorative resins, are available as either cold-cured or light-cured systems (Craig et al. 2006).

The acid-etch technique has been used to bond enamel to composite resins. The dental enamel surface is first roughened with an approximately 35% solution of phosphoric acid. A thin layer of resin of the bis-GMA type is then applied to the etched surface, and finally, the restorative resin is applied (Craig et al. 2006).

PMMA has a dominant position in denture base resins. Methacrylates are available as powder and liquid. The polymer powder is mixed with the liquid monomer. Mineral pigments are the principal coloring agents used; organic dyes less so. To avoid formation of stress cracks and to improve mechanical properties, the liquid monomer generally contains up to 10% of a cross-linking agent, usually EGDMA. Depending on the polymerization initiator used, four types of materials can be distinguished: heat-, cold-, light-, and microwave-cured polymers. In heat-cured polymers, dibenzoyl peroxide is generally used. In cold-cured polymers, the polymerization is initiated by a two-component redox system, which is usually composed of tertiary amines, e.g., N,N-dimethyl-p-toluidine, and peroxides, dibenzoyl peroxide in particular. The addition of UV stabilizers is customary to reduce discoloration. Instead of MMA, diesters of methacrylic acid with high molecular mass diols similar to bis-GMA, or high molecular mass urethane dimethacrylates are used as the monomer in light-cured polymers. The reaction of microwave-cured polymers is almost the same as for heat-cured materials. Dental technicians also use similar methacrylates in artificial teeth, crowns and bridges (Craig et al. 2006).

Orthodontic treatment corrects the position of the teeth. For removable orthodontic devices, cold-cured polymers are used. For fixed orthodontic appliances, resins very similar in chemical composition to those used in cold-cured restorative materials are employed as adhesives (Craig et al. 2006).

When commonly used dental restorative materials in the Finnish market were analyzed, bonding materials most often contained 2-HEMA and bis-GMA, the composite resins bis-GMA and TREGDMA, and glass-ionomers 2-HEMA and TMPTA (Henriks-Eckerman et al. 2004).

Dentists and dental nurses are most commonly exposed to 2-HEMA, TREGDMA, and bis-GMA, they most often react to 2-HEMA, sometimes also to TREGDMA, but rarely to bis-GMA (Goon et al. 2006; Aalto-Korte et al. 2007b). Among dental technicians, MMA and EGDMA are the most significant allergens (Aalto-Korte et al. 2007b). Reactions to 2-HPMA, tetrahydrofurfuryl methacrylate (THFMA), ethyl methacrylate (EMA), butanediol dimethacrylate (BUDMA), and urethane dimethacrylate (UDMA) are quite common among dental workers, but these reactions possibly represent cross-allergy to other methacrylates (Aalto-Korte et al. 2007b).

At FIOH in the 1980s, contact allergy to epoxy acrylates was found in five dental professionals, and was always connected with reactions to DGEBA-based epoxy resin (Kanerva et al. 1986; Kanerva et al. 1989; Kanerva and Zwanenburg 2000). These cases, along with the patch tests of other epoxy allergic patients at FIOH, indicated that exposure to DGEBA epoxy resin results in cross-reactivity to epoxy acrylates and vice versa (Kanerva and Zwanenburg 2000; Kanerva 2001). In a 1984 animal study, impurities in commercial products of bis-GMA had a high sensitizing capacity, for which the presence of epoxy resin was a probable explanation (Bjorkner et al. 1984). In 1991, dental restorative materials were analyzed at FIOH, and small amounts (0.01–0.06%) of DGEBA epoxy resin were present in all of the seven dental restorative materials that contained bis-GMA (Aalto-Korte et al. 2007b). In 2001, DGEBA epoxy resin oligomers were no longer detected in analyses of bis-GMA-containing dental materials at FIOH (Aalto-Korte et al. 2009). Although dental composite resins still contain bis-GMA, contact allergy to it was rare in a recent series at FIOH, possibly either because the products no longer contain sensitizing impurities, or because the use of gloves prevents sensitization to this high-molecular-weight compound and its possible impurities.

Patients sensitized to methacrylates may develop symptoms such as stomatitis, cheilitis, or perioral dermatitis after dental care, but these usually disappear in 1–2 weeks. The relevance of contact allergy to symptoms of longer duration and to conditions such as burning mouth syndrome is difficult to ascertain.

3.2 Artificial Nail Products

The use of artificial nails has gained much popularity in recent decades. With the increasing number of nail studios, artificial nails are nowadays among the main causes of (meth)acrylate contact allergy in developed countries (Sood and Taylor 2003; Constandt et al. 2005; Lazarov 2007; Teik-Jin Goon et al. 2007).

There are various types of artificial nails: preformed plastic nail tips (press-on nails), "silk nails," and sculptured nails, which include so-called chemically cured "acrylic nails" and photo-bonded "gel nails." Nail tips and silk nails are usually glued using cyanoacrylate products, but more sensitizing acrylic monomers may also be used. In the "acrylic nail" method, liquid monomer and powdered polymer are mixed and painted onto the nail and extension template. The liquid monomer is typically composed of EMA or another monomethacrylate, and the polymer powder usually contains PMMA or polyethyl methacrylate (PEMA). The liquid monomer is highly sensitizing, but the polymer may also contain traces of monomers, e.g., MMA and EMA (Kanerva et al. 1996). In light-cured sculptured "gel nails," the resins are similar to dental bonding resins: they are serially applied in many layers, first a primer and then the acrylic nail resin, after which the layer is cured in a "photo-bonding box," and the procedure is repeated. A primer can be composed of methacrylic acid or 2-HEMA, but traces of other undeclared monomers can also be found. The resin part is typically based on epoxy acrylates (bis-GMA) or acrylated urethane as matrix monomers in combination with mono- and polyfunctional cross-linking monomers such as TREGDMA, EGDMA, 2-HPMA, TPGDA, and 2-HEA (Kanerva et al. 1996; Sauni et al. 2008). Knowledge of the exact composition of nail acrylics is sparse.

Both nail beauticians and their customers are in danger of being sensitized to acrylic resins. Nail beauticians often wear artificial nails themselves. Allergic contact dermatitis from (meth)acrylates in artificial nails usually affects the hands, especially the fingertips. With nail customers, periungual involvement may lead to onycholysis and deformations of the nail bed, while nail technicians develop symptoms on the face and forearms more commonly than their customers (Constandt et al. 2005; Lazarov 2007). In a Belgian study of 27 nail acrylate patients, nearly all reacted to 2-HEMA, and this allergen was recommended together with ethyl cyanoacrylate (ECA) for screening contact allergy from artificial nail products (Constandt et al. 2005). Although 2-HEMA has also been among the most commonly positive allergens in other nail patient series (Lazarov 2007; Teik-Jin Goon et al. 2007), the results are difficult to compare because patients have not been tested with a similar tray of allergens and there is little information on the chemical composition of the products. In general, the nail patients have allergic reactions to the same methacrylates as the dental cases, but sensitization to cyanoacrylates, epoxyacrylates, and acrylates is also possible.

3.3 Acrylic Glues

Glues, sealants, and adhesives are a relatively common occupational source of sensitization to methacrylates and acrylates, in addition to dental restorative materials and artificial nails (Guerra et al. 1993; Geukens and Goossens 2001; Sood and Taylor 2003). Anaerobic sealants are typical glue products that cause contact allergy (Conde-Salazar et al. 1988; Guerra et al. 1993; Holme and Statham 2000; Sood and Taylor 2003; Aalto-Korte et al. 2008).

Anaerobic adhesives are mixtures of acrylic esters which remain liquid when exposed to air but harden when confined between metal surfaces. These mixtures can be used for a large number of industrial purposes such as locking threaded fasteners; sealing threaded pipe connections; retaining cylindrical machine components; sealing flange joints; bonding structural components; sealing porous metal castings, welds and powdered metal parts; and many other applications (Onusseit et al. 2010b). Anaerobic adhesive compositions usually consist of mixtures of methacrylate esters or methacrylated urethanes, initiators, accelerators, and other additives. Traditionally, methacrylate esters are polyether types based on oligomeric polyethylene or polypropylene glycols (Onusseit et al. 2010a).

In chemical analyses at FIOH, the main components of anaerobic glues were found to be TREGDMA, and diethyleneglycol dimethacrylate (DEGDMA) and 2-HPMA were used as reactive diluents (Kanerva et al. 1997). Further analyses of anaerobic products have also detected methacrylates 2-HEMA, EGDMA, tetraethyleneglycol dimethacrylate (TETEGDMA) and pentaethyleneglycol dimethacrylate (PEGDMA), and MMA (Aalto-Korte et al. 2008) and epoxyacrylate bis-GA (Aalto-Korte et al. 2009). The typical clinical picture of allergic contact dermatitis due to anaerobic glues is dermatitis of the distal fingers (Conde-Salazar et al. 1988). Typical occupations include assemblers of machines and mechanical devices, mechanics, and plumbers. The most commonly positive acrylic monomers in patients exposed to anaerobic glues have been methacrylates 2-HEMA, EGDMA, TREGDMA, and 2-HPMA (Conde-Salazar et al. 1988; Holme and Statham 2000; Aalto-Korte et al. 2008). It is noteworthy that anaerobic glues may contain epoxy acrylates bis-EMA, bis-GMA, glycidyl methacrylate, and bis-GA (Aalto-Korte et al. 2009). In the USA, three glue-related cases were positive to glycidyl methacrylate, and one of them had used an anaerobic sealant that contained glycidyl methacrylate (Dempsey 1982). Bis-GA in an anaerobic sealant had sensitized one worker in Finland (Aalto-Korte et al. 2009). These acrylated epoxies need to be tested separately, as the patients need not have contact allergy to epoxy resin or acrylates.

Two-component acrylate adhesives are cold-setting products which contain methacrylates or acrylates as the monomer, and other polymers (Onusseit et al. 2010b). There are a few reports of sensitization to methacrylates in 2-component acrylic glue products (Kanerva et al. 1995; Aalto-Korte et al. 2008). The patch-test-positive products of these patients contained methacrylates such as 2-HEMA, EGDMA and MMA, and acrylates. The reaction patterns of these patients did not essentially differ from those of other patients who had handled monocomponent anaerobic products, i.e., strong allergic reactions to many methacrylates, and milder or fewer reactions to acrylates.

Cyanoacrylate adhesives are one-component polymerization adhesives. Methyl, ethyl, butyl, and methoxyethyl esters of cyanoacrylic acid (methylcyanoacrylate, ethylcyanoacrylate, butylcyanoacrylate, methoxyethylcyanoacrylate) are used for these products; soluble polymers and plasticizers are incorporated to control viscosity, and rubbers for elastification. Cyanoacrylate adhesives rapidly polymerize to form a high molecular mass, but largely uncross-linked polymers. In most cases, atmospheric moisture, or the film of moisture on the substrate is sufficient to initiate polymerization. However, due to this sensitivity to atmospheric moisture, the adhesives must be stored in tightly sealed containers. Cyanoacrylates are used for bonding small items of nearly all substrates. Cyanoacrylate adhesives are also used in surgery and wound management (Onusseit et al. 2010b). Cyanoacrylate glues are rare sensitizers in industrial settings (Bruze et al. 1995; Conde-Salazar et al. 1998) and a few cases have been reported in nail technicians, their customers, and hair dressers (Belsito 1987; Tomb et al. 1993; Constandt et al. 2005; Lazarov 2007). Cyanoacrylates have to be tested separately as there is no cross-allergy between them and other (meth)acrylates.

UV-cured acrylic glues have also caused contact allergy (Whittington 1981; Brooke and Beck 2002; Kiec-Swierczynska et al. 2005; Minamoto and Ueda 2005). These products may contain only acrylates, and the patients may not necessarily react to methacrylates.

Orthopaedic Adhesives (Bone Cements) are used to anchor long-term implantable devices to the neighboring bone. Bone cements consist of separate powder and liquid components which are mixed prior to application. Though many products exist, the powder components always contain methacrylate polymer, a polymerization initiator, and a radiopaque medium. The liquid component contains MMA with small amounts of accelerator for the hardening process (Onusseit et al. 2010a). Contact allergy to bone cements in orthopedic surgeons and nurses is rare.

Window screen repair products are used for repairing small cracks in window screens, and the systems can be UV-cured. A windscreen repairer at FIOH, and three other previously reported cases have reacted to 2-HEMA (Bang Pedersen 1998; Banerjee et al. 2001; Geukens and Goossens 2001).

Non-occupational sources of sensitization include not only nail glues and instant adhesives but also adhesives in electrosurgical grounding plates, skin tapes, and glues in insulin pump infusion sets.

3.4 Paints, Varnishes, and Coatings

Both the workers that manufacture UV-curable paints, varnishes, lacquers, and coatings, and the workers that use these products are at risk of developing contact allergy to acrylates. Significant allergens in these products include dipropyleneglycol diacrylate (DPGDA) (Estlander et al. 1998; Isaksson and Zimerson 2007), TPGDA (Conde-Salazar et al. 2007), and 2-HEA (Geukens and Goossens 2001). Patients often react positively to various acrylates (e.g., DEGDA), but whether the reactions represent cross-allergy or primary sensitization is difficult to assess with the sparse information available on exact exposure. Paints sometimes contain methacrylates, such as 2-HEMA (Geukens and Goossens 2001). As regards wood coatings, nine cases of PETA allergy from UV-curable water-based acrylate lacquer in a furniture factory were reported in Sweden (Saval et al. 2007). The literature contains two cases of acrylate allergy from the coating of optical fibers: one caused by urethane acrylate and TMPTA (Maurice and Rycroft 1986) and another caused by phenoxyethoxy ethylacrylate (Jolanki et al. 2001). Glycidyl methacrylate, an epoxy methacrylate used in the coating of spectacle lenses, caused allergic contact dermatitis in Spain (Sanchez-Perez et al. 2008). In Finland, TMPTA used in the manufacture of printed circuit boards induced dermatitis in one worker (Kanerva et al. 1998).

3.5 Printing Work

Radiation-curable inks are applied to metal, paper, wood, and plastics. Lithographic (offset) and screen printing inks are the main printing inks, while flexographic inks, intaglio inks, and ink-jet printing are also common. In the printing industry, flexographic printing plates are also manufactured from UV-curable materials (Streitberger et al. 2010). In earlier reports of allergic contact dermatitis from UV-cured inks, patients were often exposed and sensitized to TMPTA and PETA (Emmett and Kominsky 1977; Bjorkner et al. 1980; Isaac et al. 1992). In later reports, TPGDA and/or epoxyacrylates bis-GA and bis-GMA have been the primary allergens (Goossens et al. 1998; Scotnicki and Pratt 1998; Kanerva et al. 2000). The main allergens in UV-curable printing inks are thus acrylates and epoxyacrylates, but methacrylates can also be used: 2-HEMA together with diaminodiphenylmethane and triglycidylisocyanurate were the causes of allergic dermatitis in a silk-screen printer in the manufacture of circuit boards (Jolanki et al. 1994). Sensitizing acrylamide derivatives are used in printing plates work (see below ➲ Sect. 3.7), as is 2-HEMA (Pedersen et al. 1983).

3.6 Allergic Contact Dermatitis from Epoxyacrylates

Allergic reactions to bis-GMA, bis-GA, glycidyl methacrylate, and bis-EMA are usually seen in patients with allergic contact dermatitis from DGEBA epoxy resin, who are exposed to only epoxy resin products. About 20% of patients who are allergic to DGEBA epoxy resin react to some of the chemicals, most often to bis-GA and bis-GMA (Lee et al. 2002; Aalto-Korte et al. 2009). The majority of the reactions to epoxyacrylates probably represent cross-allergy, but some patients, however, are sensitized as a result of specific exposure. In particular, allergic reactions to bis-GA without concomitant DGEBA epoxy resin allergy point to specific sensitization. To detect the specific contact allergy, these compounds should be tested separately, because the patients do not necessarily have a concomitant allergy to DGEBA epoxy resin or acrylates.

UV-cured printing inks are a significant source of bis-GA sensitization (Emmett and Kominsky 1977; Bjorkner et al. 1980; Nethercott et al. 1983; Guimaraens et al. 1994; Kanerva et al. 2000; Aalto-Korte et al. 2009), and bis-GA in the production of UV-cured paints has sensitized one patient (Jolanki et al. 1995). In these cases, specific exposure to bis-GA led to specific sensitization without allergy to DGEBA epoxy resin. At FIOH, an assembler of hydraulic devices was investigated. He developed dermatitis while using anaerobic sealants, and in patch tests, he reacted to 2-HPMA and bis-GA, but not to epoxy resin. In the chemical analysis, bis-GA was detected in one of his sealants at an 8% concentration (Aalto-Korte et al. 2009). The literature nevertheless presents many bis-GA-positive cases with no shown specific exposure, but these patients usually have allergic reactions to DGEBA epoxy resin and bis-GMA (Kanerva et al. 2000; Lee et al. 2002; Aalto-Korte et al. 2009). The majority of the reactions probably represent cross-allergy.

Bis-GMA was introduced as a component of dental composite resin in the 1960s. Since then it has been widely found in products used by dentists (Estlander et al. 2006), denture materials (Kanerva et al. 1993; Aalto-Korte et al. 2007b), artificial nail preparations (Hemmer et al. 1996; Geier et al. 2007; Sauni et al. 2008), and in printing work (Goossens et al. 1998). According to the Finnish Product Register, it was also found in some adhesives, in a wind screen repair resin, and in a filler for motor vehicles (Aalto-Korte et al. 2009). Contact allergy to bis-GMA has been reported in dental workers (Kanerva et al. 1986; Kanerva et al. 1989; Rustemeyer and Frosch 1996; Kanerva and Zwanenburg 2000; Geukens and Goossens 2001;

Wrangsjo et al. 2001; Sood and Taylor 2003; Goon et al. 2006), dental patients (Kanerva and Alanko 1998; Lee et al. 2002; Goon et al. 2006), a printer (Bong and English 2000), a silk-screen maker (Goossens et al. 1998), and a mechanic handling coating materials (Kanerva et al. 2000). The allergic reactions to bis-GMA in these studies usually occurred concomitantly with an allergic reaction to the DGEBA epoxy resin. Many of the previously reported dental patients and the mechanic were reported to have been sensitized to DGEBA epoxy resin before developing symptoms from materials containing bis-GMA (Kanerva and Alanko 1998; Kanerva et al. 2000; Lee et al. 2002). In a German study, six (15%) out of 40 bis-GMA positive patients did not react to DGEBA epoxy resin, and the only probable bis-GMA exposure was to artificial nails in one patient (Geier et al. 2007). At FIOH, all bis-GMA-positive patients also reacted to DGEBA epoxy resin. In the literature, 10–18% of the epoxy resin allergic cases had had an allergic reaction to bis-GMA (Lee et al. 2002; Geier et al. 2007; Aalto-Korte et al. 2009). Bis-GMA per se has either low sensitizing capacity or none at all (Bjorkner et al. 1984). The probable explanation for concomitant reactions is a cross-allergy between DGEBA epoxy resin and epoxy (meth)acrylates (bis-GMA and bis-GA) (Kanerva et al. 2000; Lee et al. 2002; Geier et al. 2007; Aalto-Korte et al. 2009).

Glycidyl methacrylate was reported to be the cause of occupational allergic contact dermatitis in a chemist who impregnated paper and textile materials to make them water- and oil-resistant (Matura et al. 1995), and in Sweden an allergic patch test reaction to glycidyl methacrylate was seen in a production worker in a paint binder factory which used the chemical (Gruvberger et al. 1998). In the USA, three glue-related cases were positive to glycidyl methacrylate, and one of them had used an anaerobic sealant that contained glycidyl methacrylate (Dempsey 1982). In Spain, a worker developed occupational allergic contact dermatitis due to glycidyl methacrylate in a liquid that was used in coating spectacle lenses (Sanchez-Perez et al. 2008). None of the six patients were reported as having DGEBA epoxy resin allergy. One case of chemical burn from glycidyl methacrylate has recently been reported (Shimizu et al. 2008). Glycidyl methacrylate is an ester of methacrylic acid and epichlorohydrin; it has a methacrylate structure at one end of the molecule and an epoxy group at the other. At FIOH, in a series of ten patients with allergic reactions to glycidyl methacrylate, the majority of the cases also reacted to DGEBA epoxy resin in the baseline series, and had been occupationally exposed to epoxy products. At FIOH, however, no specific exposure to glycidyl methacrylate was found (Aalto-Korte et al. 2009).

In the Finnish Product Register of Chemicals, bis-EMA appears in numerous glues and in some dental products. In the literature, some cases of allergic reactions to bis-EMA are reported, many of them in dental personnel, often with a simultaneous reaction to the DGEBA epoxy resin and bis-GMA. However, in the literature there are no detailed descriptions of primary sensitization with known exposure to bis-EMA. At FIOH, a manicurist with allergic reactions to bis-EMA and glycidyl methacrylate was investigated, but these compounds were not mentioned in the product declarations, and the products were not analyzed (Aalto-Korte et al. 2009).

Allergic reactions to bis-MA have also been reported in single dental workers. Cross-allergy to epoxy resin does not seem to be common, as 41 epoxy-resin-allergic patients remained negative to this substance in the USA (Lee et al. 2002). In 2008, a search in the Finnish Chemical Register of Chemicals yielded no products containing bis-MA (Aalto-Korte et al. 2009).

3.7 Allergic Contact Dermatitis from Acrylamide Derivatives and Acrylonitrile

Acrylamide used in polyacrylamide gel electrophoresis may cause allergic contact dermatitis in exposed workers (Lambert et al. 1988; Dooms-Goossens et al. 1991; Beyer and Belsito 2000; Aalto-Korte et al. 2002). Piperazine diacrylamide, a cross-linker of acrylamide gel electrophoresis, can also sensitize (Bjorkner 2006). Secondary acrylamides such as N,N'-methylene-bis-acrylamide (MBAA), have been identified as sensitizers in photo polymerizing printing plates (Malten et al. 1978; Pedersen et al. 1982; Pedersen et al. 1983). Patients sensitized to the secondary acrylamides used in Nyloprint® printing plates may react to acrylamide on patch testing (Pedersen et al. 1982). Although printing plates may contain other (meth)acrylic monomers, the patients may have monosensitization to secondary acrylamides and thus do not react to commonly tested acrylic monomers.

A few cases of allergic contact dermatitis from acrylonitrile have been reported (Bjorkner 2006).

4 Patch Testing with Acrylic Resins

It is common that (meth)acrylate-allergic patients have simultaneous allergic reactions to several (meth)acrylate test substances, although they have probably not been exposed to all the positive compounds. Some of the multiple reactions probably derive from cross-allergy between acrylic monomers. However, it is difficult to establish an individual's history of exposure to various acrylic monomers in acrylic products, as he/she will have used various different products during their work life. Acrylic products often contain many undeclared acrylic monomers, and differences probably occur between different batches of the same product (Kanerva 2001; Henriks-Eckerman et al. 2004). When commonly used dental restorative materials in the Finnish market were analyzed, SDSs proved to be unreliable: information regarding methacrylates was provided in only half of the products which, according to the analysis, contained methacrylates. Moreover, some methacrylic compounds given in the safety data sheets could not be detected (Henriks-Eckerman et al. 2004). Impurities in patch test preparations may also have led to false interpretations of patch test results: for instance, in the 1980s technical grade raw materials were sometimes used in commercial test preparations (Kanerva et al. 1989). Many problems with test substances still remain to be solved, e.g., Chemotechnique declares that their aromatic urethane acrylate (ar-UDA) contains some PETA and pentaerythritol tetraacrylate. Sensitization to PETA explains reactions to ar-UDA.

In all larger patient materials, methacrylates 2-HEMA, EGDMA, and 2-HPMA have been among the most commonly positive allergens (Tucker and Beck 1999; Geukens and Goossens 2001; Sood and Taylor 2003; Aalto-Korte et al. 2007b; Teik-Jin Goon et al. 2007). These three allergens are significant for patients exposed to dental products, glues and artificial nails, products which usually contain methacrylates and often epoxyacrylates, but seldom acrylates (Aalto-Korte et al. 2007b; Aalto-Korte et al. 2008). The methacrylate-exposed patients often react not only to the cross-reacting 2-HEMA, EGDMA, and 2-HPMA, but also to other methacrylates, such as MMA, EMA, TREGDMA, and THFMA. Reactions to acrylates occur, but are not very common. Patients with strong allergic reactions to some methacrylate(s) tend to react to large numbers of methacrylates, as well as to some acrylates. The most commonly positive acrylates in methacrylate-exposed patients are EA, TREGDA, and DEGDA.

Contact allergy to acrylates is not as common as allergy to methacrylates. There are no large published materials on acrylate allergy, and in the available small series the relative importance of different acrylate allergens depends on the products the patients have been exposed to. Among the patients investigated at FIOH were several cases in which acrylate contact allergy was limited to the chemical the patients were exposed to, and the patients exposed solely to acrylates did not react to methacrylates. Thus, the results of FIOH imply that although exposure to methacrylates might induce cross-reactivity to acrylates, exposure to acrylates does not usually lead to cross-sensitization to methacrylates. Guin's textbook presents similar cross-reactivity rules concerning monoacrylates and monomethacrylates (Guin and Work 1995). The acrylate-allergic patients at FIOH were mainly exposed and sensitized to diacrylates (TPGDA, DPGDA, DEGDA, and TREGDA), but not to monoacrylates to the same extent. Multiple reactions to several acrylates are also quite common, which imply a cross-allergy between them. When clinical patients are analyzed, it is difficult to draw firm conclusions regarding cross-allergy, because concomitant exposure to several acrylic monomers is always an alternative explanation.

While the pattern of concomitant reactions in methacrylate-exposed patients varies only slightly according to the type of exposure, the diagnosis of contact allergy to acrylates, epoxyacrylates, cyanoacrylates, and acrylamide derivatives often requires testing with the specific allergen.

At FIOH in the 1980s, acrylates EA, 2-HEA, and 2-HPA caused active sensitization in several patients when tested at concentrations of 0.5–1% (Kanerva et al. 1988). The present recommended concentration for acrylates is 0.1% in petrolatum, and most methacrylates are tested at a concentration of 2%. Late reactions appearing after D7 are not necessarily due to active sensitization (Isaksson et al. 2005), and reactions to low concentrations and to cross-reacting secondary allergens in particular tend to appear later.

When testing patients' own products, the concentration of the methacrylate/acrylate product should be adjusted to the concentrations of the monomers in the product so that 2% for any sensitizing methacrylate monomer or 0.1% for any sensitizing acrylate monomer is not exceeded (Jolanki et al. 2000a). At FIOH, no active sensitizations to patients' own products have been observed (Aalto-Korte et al. 2007a). The recommendation for cyanoacrylates is 10% in petrolatum. Testing acetone dilutions of cyanoacrylates in aluminum chambers yields false negative results. Acetone dilutions may be used in plastic-coated aluminum chambers (Bruze et al. 1995). At FIOH cyanoacrylate glues are tested as is, dried in Finn-Chambers due to the simplicity of the procedure (Aalto-Korte et al. 2008).

5 Skin Irritation and Other Effects

Acrylic acid is moderately toxic and very corrosive. The vapor is an irritant to the eyes and respiratory tract, and skin contact may cause burns. Acrylic esters are of moderately acute toxicity, which decreases as the number of carbon atoms in the alkyl group increases. Generally speaking, methacrylates are less toxic than their corresponding acrylates. The mucous membranes of the eyes, nose, and throat are particularly sensitive to irritation. Acrylic monomers can produce eye and skin irritation ranging from slight to corrosive, depending on the monomer and the type of exposure. Liquid methyl and ethyl acrylates severely irritate the skin and mucous membranes, and are corrosive to the eyes, whereas the butyl and 2-ethylhexyl acrylates have less severe effects. Methyl and ethyl acrylate vapors are very lachrymatory, extremely irritating to the respiratory tract, and corrosive to the eyes, causing corneal injury. The lachrymatory effect of the butyl and 2-ethylhexyl esters is weak. Methacrylic acid is more corrosive than its esters (Bauer 2010; Ohara et al. 2010). Handling methacrylate products has caused respiratory problems, rhinitis, and asthma in dental workers and nail technicians.

In humans and laboratory animals, single or repeated exposure to acrylamide caused local irritations on contact with the skin and neurological symptoms. The peripheral neuropathy is a result of long-term accumulation and appears after a latent period. Acrylamide is readily absorbed during oral, inhalation, and dermal exposure. Its genotoxicity, the formation of the genotoxic metabolite glycidamide in humans, and long-term animal studies, indicate that acrylamide has the potential to cause cancer in humans. Accordingly, acrylamide has been classified as probably carcinogenic to humans (Ohara et al. 2010).

6 Prevention

Protection required for the safe handling of acrylic acid and methacrylic acid and their esters includes chemical-resistant gloves and clothing, splash-proof goggles, and effective ventilation of the workplace. Small molecular acrylic compounds permeate common disposable natural rubber and vinyl gloves rapidly. In dental care, at least double gloving with thin vinyl or natural rubber gloves should be used for a 15-min task. For a task lasting 15–30 min, good nitrile rubber gloves should be used, preferably as a double layer with other gloves. A simple polyethylene glove under another glove may improve protection considerably when performing longer work tasks. Double gloving becomes easier if the inner gloves are of a larger size (Mäkelä and Jolanki 2005). The development of so-called no-touch techniques in the application of dental composite resins (e.g., pistols and syringes) has most likely played a significant role in the prevention of sensitization to methacrylates; at least in Finland, methacrylate allergy in dentists and dental nurses is no longer as common as it was in the 1990s. Furthermore, most workers in these two occupations are aware of the rapid permeation of gloves to small methacrylates, and many of them change gloves immediately when they notice glove contact with materials containing methacrylate.

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