

Occupational contact allergy to (meth)acrylates

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Among 13,833 patients suspected of contact dermatitis examined during the years 1978–1999, occupational contact allergy to (meth)acrylates was diagnosed in 31 patients. The 3 most common sensitizers were ethyleneglycol dimethacrylate (17 positive patch tests), 2-hydroxyethyl methacrylate (14) and triethyleneglycol dimethacrylate (6). The aim of this report was to assess the different occupations and industries responsible for occupational sensitization to (meth)acrylates. 14 of the 31 patients work in the dental sector, either as a dentist or as a student of dental technology, where (meth)acrylate-containing dental prostheses and dental composites are mainly responsible for allergy to (meth)acrylates. An increasing trend in dermatological problems related to the expansion of the use of (meth)acrylates is clearly reflected in the patient population of our dermatology department.

Key words: allergic contact dermatitis; acrylates; methacrylates; occupational; airborne. © Munksgaard, 2001.

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Since their development in the 1930s, the use of acrylates and methacrylates has expanded enormously. This has resulted in a vast range of acrylate-containing products for both occupational and non-occupational purposes. The acrylates belong to the class of synthetic plastics and resins. They form a large group of chemical components that have acrylic acid as their common basis. Acrylic acid is a carboxyl acid group bonded to a vinyl group ($\text{CH}_2=\text{CH}-$). Acrylates are synthesized by a polymerization reaction in which the vinyl group intervenes as a reactive group.

Consequent upon their introduction, case studies of contact allergy to (meth)acrylates began to appear in the literature. In 1947, Stevenson (1) and Moody (2) were the first to report an occupationally acquired allergic contact dermatitis, the patient being a dental technician. The non-polymerized products are the most allergenic, whereas the end-products obtained after polymerization have little or no allergenic capacity.

Patients and Methods

In the period from 1 January 1978 through 31 December 1999, the Contact Allergy Unit of the Dermatology department of the Katholieke Universiteit Leuven tested 13,833 patients for contact allergy by means of patch tests. These patch tests

were conducted with Van Der Bend[®] patch-test chambers applied to the back of the patient with Micropore[®] and fixed with Fixomull[®] (Biersdorf) and later on with Mefix[®] (Mölnlycke) as adhesive tape. The patch-test chambers were removed after 2 days (D). Readings were made at D2 and at D3 or D4, and sometimes also later. A standard series, to which certain substances were added, was used with all the patients. Depending on the patient's individual history, other series, as well as the material and substances with which the patient came in contact at work, were included, if they seemed relevant. The vehicles and test concentrations of the (meth)acrylates are given in Table 1. All acrylate-containing products, such as composite resins, gels, varnishes, inks and paints, were tested semi-open as is (3).

Results

Of all the patients in whom patch tests were conducted, 7369 (53.3%) showed a contact allergy to 1 or more substances. A positive patch test to 1 or more (meth)acrylates was observed in 54 patients: 23 of the contact allergies to (meth)acrylates were of non-occupational, and 31 of occupational, origin. Only the occupationally-induced contact allergies to (meth)acrylates will be discussed further here.

Table 1. Abbreviations and patch test concentrations of (meth)acrylates

1. 2-EHA	2-ethylhexyl acrylate	0.5% pet.
2. 2-HEA	2-hydroxyethyl acrylate	2% pet.
		1% pet.
3. 2-HEMA	2-hydroxyethyl methacrylate	2% pet.
4. MMA	methyl methacrylate	2% pet.
5. HDDA	hexanediol diacrylate	1% pet.
		0.1% pet.
6. BA	butyl acrylate	1% pet.
		2% pet.
7. BUDMA	1.4-butanediol dimethacrylate	2% pet.
8. BUDA	1.4- butanediol diacrylate	2% pet.
9. EGDMA	ethylene glycol dimethacrylate	2% pet.
10. TREGDMA	triethylene glycol dimethacrylate	2% pet.
		1% pet.
11. TEGDMA	tetraethylene glycol dimethacrylate	1% pet.
		0.1% pet.
12. TPGDA	tripropylene glycol diacrylate	1% pet.
		0.1% pet.
		0.01% pet.
13. bis-GMA	2,2-bis(4-(2-hydroxy-3-methacryl-oxypropoxy)-phenyl)propane	2% pet.
14. bis-EMA	2,2-bis(4-(methacryloxyethoxy)-phenyl)propane	2% pet.
15. PETA	pentaerythritol triacrylate	1% pet.
		0.1% pet.
16. TMPTA	trimethylolpropane trimethacrylate	0.1% pet.
17. UEDMA	urethane dimethacrylate	1% pet.
18. GMA	glycidyl methacrylate	0.05% pet.
19. EEA	ethoxy ethylacrylate	0.05% pet.
20. bis-MA	2,2-bis(4-(methacryloxy)phenyl)propane	2% pet.
21. N,N-dimethylamino-ethyl methacrylate		2% pet.
22. acrylamide		5% aq.
23. epoxy acrylate		0.5% pet.
24. tert. BA	tertiary butyl acrylate	0.5% pet.
		1% pet.

The main characteristics of the patients diagnosed with occupational contact dermatitis from (meth)acrylates are given in Table 2. Only 14 patients mentioned wearing gloves in their occupational practice. Latex, cotton, nitrilbutyl rubber and PVC gloves were used. One patient used 4H gloves but wore them longer than 4 h. In 4 patients, the localization of the lesions supported the possi-

bility of an airborne dermatitis. One dentist complained of sensation disturbance on the fingertips. Rhinitis, conjunctivitis, wheezing and dyspnoea in relation to the use of (meth)acrylates were mentioned once.

Which acrylates and methacrylates function as allergens?

In the course of the period 1 January 1978 and 30 June 1999, patch tests were conducted with 26 different acrylates and methacrylates. Contact allergy to 20 different (meth)acrylates was diagnosed.

The 3 (meth)acrylates responsible for most of the positive patch tests are EGDMA, 2-HEMA and TEGDMA. These 3 methacrylates are responsible for 27 of the 72 positive patch tests (Table 3).

In what occupations and industries is contact allergy to (meth)acrylates found?

The different occupations and industries responsible for occupational sensitization to (meth)acrylates are given in Fig. 1.

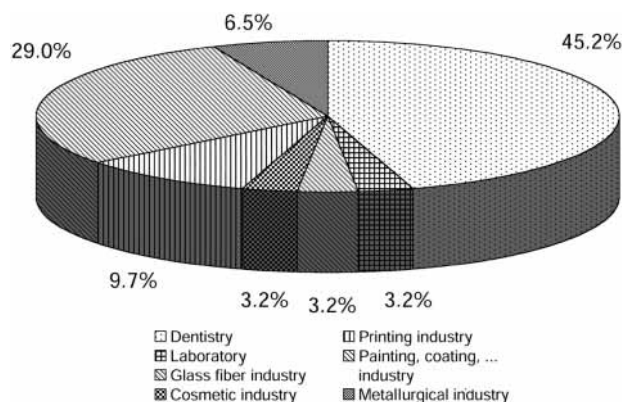


Fig. 1. The different occupations and industries responsible for occupational sensitization to (meth)acrylates.

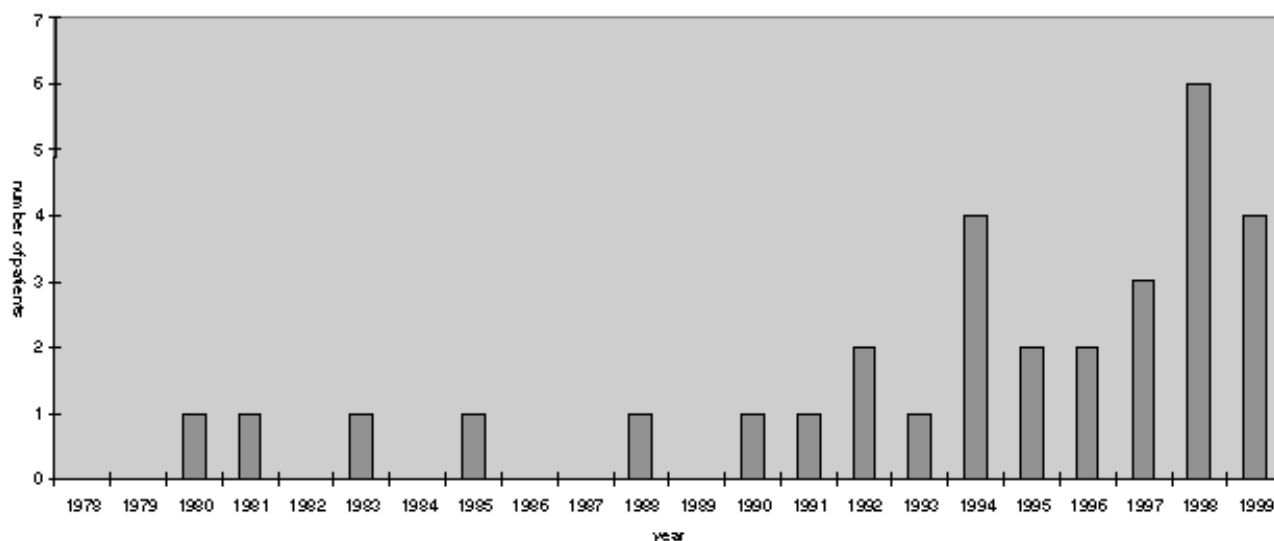


Fig. 2. Evolution in time of number of patients with occupational contact allergy to acrylates.

Evolution over time of occupational contact allergy to (meth)acrylates

In the 1990s a larger number of patients were diagnosed per year than in the 1980s. In 1998 we recorded the largest number of patients of all (Fig. 2).

Sex and age

8 of the 31 patients are women. The average age of the patients in whom we diagnosed an occupational contact allergy is 36.8 years.

Discussion

Of the (meth)acrylates tested, EGDMA caused the largest proportion of positive patch tests. EGDMA tested positively 17 times. Of these patients, 11 were dentists, who accounted for almost $\frac{1}{2}$ of the patient population with occupational allergy to (meth)acrylates. The high frequency of positive patch tests to EGDMA is because this substance is used a great deal in dentistry (7, 8), for example, as a liquid component of dental prostheses as well as in dental composites (9). TREGDMA was positive 6 times.

Dimethacrylates, according to Björkner (10) and Parker (11), have little sensitizing capacity when tested in guinea pigs, while Cavelier (12) has reported that EGDMA, DEGDMA, TREGDMA and TGGDMA are moderate allergens in the guinea-pig maximization test. Several cases of contact allergy to EGDMA are described in the literature. Thus, the allergenic potential of the dimethacrylates is still a matter of discussion. The results of the present study support Cavelier, and the

many case studies in the literature reporting dimethacrylates as the causal contact allergens.

2-HEMA is 2nd. Here, too, the situation is not unambiguous. Indeed, 2-HEMA seems to be a weak allergen in guinea pigs (11). However, in the literature, 2-HEMA is reported to be the causal contact allergen in the most divergent applications. It is used very often.

14 of the 31 patients work in dentistry, either as a dentist or as a student of dental technology, where (meth)acrylate-containing dental prostheses and dental composites are mainly responsible for contact allergy to (meth)acrylates. This indicates the certain need for preventive measures in these occupations. The prospective dentist or dental technician (13) is exposed to acrylates very early in their training. Sensitization to acrylates can occur even before one is aware of the allergenic capacity of these products.

7 of the 31 patients can be classified in the group of patients where sensitization to (meth)acrylates is due to the use of paints, lacquers, varnishes, resins, glues, coatings and adhesives (14–17). Contact allergy can occur during the production process of these (meth)acrylate-containing products, but also while using the finished products, for example the use of spray paint for automobile components. Note that this group of patients covers a large group of industries and that 'overlap' with other industries given in Fig. 1 is possible.

There were also 3 patients with occupational contact allergy to (meth)acrylates, working in the printing industry. The 2 main sources of contact allergy in the printing industry are the UV-curing inks (18) and the photopolymer prints (19). The most important allergens in UV-curing inks are the multifunctional acrylates: PETA, TMPTA and

Table 2. Case reports

	Sex	Age (years)	Occupation	Year of diagnosis	Location of lesions	Positive patch tests to (readings D2/D3 or D4)
1.	M	40	salesman of UV-cured varnishes	1980	periorally, periorbitally, back of hands	PETA +++/+++ HDDA +++/+++ BA +++/++ tert. BA +++/++ varnish ++++/+++
2.	M	35	dentist	1981	tips of fingers of both hands	MMA +++/+
3.	M	30	dentist	1983	face and both hands	tooth impression material +++/++ BUDMA +++/++ EGDMA +++/++ TEGDMA +++/++ MMA +++/++ components of front fillings +/+/-
4.	M	32	worker in photo-gravure company	1985	digits 1, 2, 3 and 4 of both hands	MMA +++/++ HDDA +++/++ scraping of Nyloprint® ++++/+++
5.	F	25	student in lab for immunological research (polyacrylamide electrophoresis)	1988	fingers, right wrist, extensor side of left forearm	acrylamide +++/++ stock solution (containing acrylamide and N,N'-methylenebisacrylamide) +/+/-
6.	M	31	dentist	1990	fingertips of both hands	TEGDMA +++/++ EGDMA +++/+++ BUDMA +++/++ components of front fillings +/+ +
7.	M	19	dental technician (student)	1991	backs of both hands, fingertips, palm of left hand	TEGDMA -/+ + EGDMA +/+ +
8.	M	47	demonstrator of application of artificial gel nails	1992	palms of both hands, fingertips, face and neck	2-HEMA +++/++ UV-cured gel (containing 2-HEMA) +/+
9.	M	29	worker treating parquet floors	1992	both hands and intermittently on the feet when resin material had been spilled	EGDMA -/+ + 2-HEMA -/+ + acrylate resin products used +/+ -
10.	M	32	chemist (using acrylates to make paper and textiles water and oil resistant)	1993	backs of both hands, digits 1, 2 left and digits 3, 4 right	glycidyl methacrylate +++/+++ EEA +++/+++
11.	M	50	dentist	1994	fingers of both hands	2-HEMA +++/+++ EGDMA +/+ +
12.	F	43	dentist	1994	palmar side of the fingertips 1, 2 and 3 of both hands	MMA +++/+++ MA +++/++ TEGDMA +++/+++ composite materials +++/-
13.	M	55	dentist	1994	fingertips 1, 2 and 3 of both hands	2-HEMA ++++/+++ EGDMA ++++/+++ N,N dimethylaminoethyl methacrylate +++/++ composite materials +/+ -
14.	M	39	worker in the metal-processing industry (assembled compressors)	1994	forearms	TEGDMA +++/+++ EGDMA +++/+++ Loctite® (577, 641, 242, 510) (containing EGDMA) +/+ +
15.	M	50	dentist	1995	digits 1, 2 and 3 of both hands	TEGDMA ++++/+++ Bis-GMA -/+ + Bis-EMA -/+ + BUDMA +++/++ EGDMA ++++/+++ 2-HEMA ++++/+++ urethane-dimethacrylate +/+ +
16.	M	39	worker in the plastics industry	1995	face, neck and forearms	2-HEMA +/+ + EGDMA +/+ + resins (containing multifunctional acrylates) -/+ +

Table 2 (cont'd)

	Sex	Age (years)	Occupation	Year of diagnosis	Location of lesions	Positive patch tests to (readings D2/D3 or D4)
17.	M	40	worker in a silk-screening firm	1996	palms of both hands	EGDMA +++(+) Bis-GMA +++(+) TPGDA +++ Saatigraaf 3034 [®] (containing TPGDA) ++ 2-HEA +++/- white paint (containing 2-HEA) +++
18.	M	29	body worker (using spray paint for automobile components)	1996	both hands, both forearms and face	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
19.	M	49	dentist	1997	fingertips of digits 1, 2 and 3 of both hands	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
20.	F	31	dentist	1997	both wrists and hands, the face, the neck and behind the ears	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
21.	M	38	printer (high pressure process using UV-cured inks)	1997	both forearms, face, abdomen and legs	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
22.	F	37	dentist	1998	back of the right hand, fingertips	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
23.	M	17	dental technician (student)	1998	interdigital, palmar side of fingers	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
24.	M	25	worker in the automobile industry (windscreen), using glues and paints	1998	both hands, periorbitally	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
25.	F	25	worker in a paint factory	1998	both eyelids, the neck and both wrists	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
26.	M	42	worker on building sites, using epoxy resins and glues	1998	both arms, neck and conjunctivitis	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
27.	M	54	body worker, using glues, hardeners, anti-freeze, ...	1998	palm of the left hand, inner side of the left forearm	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
28.	M	41	dentist	1999	the inner side of the right forearm, back of the right hand, the inner left arm, the neck and the occiput	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
29.	M	31	worker in the fiber glass industry	1999	palms of both hands, the neck, both forearms and the palmar side of the fingers	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
30.	M	44	worker in a firm constructing doors (using glues)	1999	both hands and arms, the neck	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-
31.	F	41	dentist	1999	fingertips of digits 1, 2 and 3 on the left hand	2-HEMA +++ EGDMA +++ 2-HEMA +++ EGDMA +++ N,N-dimethylaminoethyl methacrylate -/+ HDDA +++ antipicking paste -/+ used varnish +/-

HDDA. In printing the most important allergens are otherwise 2-HEMA and N,N'-methylenebisacrylamide.

In connection with the cosmetic industry, contact allergy to (meth)acrylates is mainly of non-occupational origin from the use of artificial nails, nail lacquer and other (meth)acrylate-containing nail products (20). The use of polyacrylamide gel in electrophoresis is also a source of sensitization to acrylates (21).

The patient working in the fiberglass industry showed an allergy to 2-HEMA and to EGDMA. Although the precise relevance is not clear, there

was a clear link between the patient's work and the dermatitis. Until now, no connection has been reported between contact allergy to (meth)acrylates and the fiber-glass industry in the international literature. We did not observe an occupational contact allergy among orthopaedists and orthopaedic nurses caused by contact with acrylate-setting plaster (22).

As regards the male-female ratio, it can be noted that occupational activities in which contact allergy to acrylates is observed are mainly attuned to the male population.

Beside contact dermatitis, other reactions to

Table 3. (Meth)acrylates causing occupational contact allergy (listed in order of importance)

Name of the (meth)acrylate	Number of positive patch tests	% of positive patch tests
1. ethylene glycol dimethacrylate	17	23.5
2. 2-hydroxyethyl methacrylate	14	19.4
3. triethylene glycol dimethacrylate	6	8.3
4. methyl methacrylate	5	6.9
1,4 butanediol dimethacrylate	5	6.9
5. N,N-dimethylaminoethylmethacrylate	3	4.2
hexanediol diacrylate	3	4.2
bis-GMA	3	4.2
epoxy acrylate		
6. hydroxyethyl acrylate	2	2.8
bis-EMA	2	2.8
7. acrylamide	1	1.4
ethoxyethylacrylate	1	1.4
bis-MA	1	1.4
urethane dimethacrylate	1	1.4
glycidyl methacrylate	1	1.4
pentaerythritol triacrylate	1	1.4
butyl acrylate	1	1.4
tertiary butyl acrylate	1	1.4
tripropylene glycol diacrylate	1	1.4
Total	72	

(meth)acrylates have been observed and described in the literature: complaints of paraesthesia of the fingertips, rhinitis, conjunctivitis, dyspnoea and wheezing after the use of (meth)acrylates has been seen in our patients. Furthermore, cases of neurological, respiratory and other dermatological reactions (irritation, contact urticaria) have also been reported (23–25).

With expansion of the use of (meth)acrylates, one can expect an increase in the dermatological problems related to their use (26, 27). This trend is clearly reflected in the patient population of our dermatology department.

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