

• CONTRIBUTIONS TO THIS SECTION MAY NOT UNDERGO PEER REVIEW, BUT WILL BE REVIEWED BY THE EDITOR •

A new stonemasonry surface adhesive causing occupational allergic contact dermatitis resulting from methyl methacrylate

Claire Higgins, Jennifer Cahill and Rosemary Nixon

Occupational Dermatology Research and Education Centre, Skin and Cancer Foundation Inc., Carlton, Victoria 3053, Australia

doi:10.1111/cod.12397

Key words: bonding agent; contact allergy; hand dermatitis; patch test; stonemason; surfacing industry; methyl methacrylate.

Allergic contact dermatitis (ACD) caused by methacrylates is most commonly described in nail technicians, orthopaedic surgeons and dental professionals. Here, we report two stonemasons from the same workplace with occupational ACD caused by methyl methacrylate (MMA) in a newly introduced surface bonding agent.

Case Reports

Case 1

A 39-year-old non-atopic male stonemason presented with a 3-month history of an intensely pruritic vesicular rash associated with fissuring on both hands. His work involved assembling stone kitchen benchtops with a surface adhesive at a company that produced high-end marble and reconstituted stone products for kitchens and bathroom vanities. Some 5 months previously, the company had replaced a polyester-based glue used for many years in the workplace with an epoxy-modified MMA adhesive, Integra Surface Bonder Xi, manufactured in Canada. This dual-cartridge glue contained 35–50% wt/wt MMA in the first cartridge, and a bisphenol A-based liquid epoxy resin, benzoyl peroxide and tricresyl phosphate in the second cartridge (1). It was applied to the stone by use of a hand-held dispensing gun with an automatic static mixer/dispensing system

that eliminated hand mixing. Excessive amounts of glue were removed with a spatula. After the glue had cured (~5 min), the stone was ground and polished; and this appeared to liberate the glue, as it could be smelt in the air. The skin symptoms improved when the patient was away from the workplace, but within hours of returning he became itchy on exposed skin, including his face. Subsequently his dermatitis recurred. He wore a single pair of disposable nitrile gloves and a dust mask when working with the glue. He had been treated with clobetasol 0.05% ointment and oral prednisolone, with only short-lived improvement.

Patch tests were performed with the Australian Baseline Series (2), the epoxy series, tricresyl phosphate, benzoyl peroxide, and the acrylate/methacrylate series (allergEAZE™ by SmartPractice®, Phoenix, AZ, USA; and Chemotechnique, Vellinge, Sweden), plus the patient's own products. We were not able to test with the glue itself. Testing was performed with allergEAZE™ Patch Test Chambers (Smart Practice®) on Scanpor® tape (Norges-plaster A/S, Vennesla, Norway), according to ICDRG criteria. The patient developed a + reaction at day (D)2 and D4 to MMA 2% pet. (CAS no. 80-62-6). He also reacted to 2-hydroxyethyl methacrylate (2-HEMA), ethylene glycol dimethacrylate (EGDMA), and 2-hydroxypropyl methacrylate (2-HPMA), all 2% pet. He was diagnosed with occupational allergic contact dermatitis (ACD) caused by MMA contained in the Integra adhesive. His dermatitis improved with avoidance of the glue.

Correspondence: Dr Claire Higgins, Occupational Dermatology Research and Education Centre, Skin and Cancer Foundation Inc., Level 1, 80 Drummond Street, Carlton, Victoria 3053, Australia. Tel: +61 3 9623 9400. E-mail: chiggins@occdern.asn.au

Conflict of interests: The authors declare no conflict of interests.

Case 2

A 44-year-old non-atopic male stonemason from the same workplace presented with a 4-week history of

pruritic, tender dermatitis on both hands. He had also started using Integra Surface Bonder Xi several months previously. He had a long history of psoriasis, for which he took methotrexate and acitretin, and had a history of reacting to cheap jewellery. On examination, he had scaling and erythema involving his fingers and palms. Psoriasis was mainly located on his elbows. He had used mometasone furoate 0.1% ointment with limited improvement. Daivobet® ointment had caused skin irritation.

Patch testing was performed as described above. The patient developed a + reaction at D2 and D4 to MMA. He also had positive reactions to 2-HEMA, EGDMA, triethylene glycol dimethacrylate, and tetrahydrofurfuryl methacrylate (all 2% pet.), and to nickel. He was also diagnosed with occupational ACD caused by MMA in the Integra adhesive. Both men were advised to avoid further contact with the adhesive, and their employer reacted swiftly by limiting use of the glue to a particular area of the factory and instituting enhanced skin protective measures.

Discussion

This is a case of an old allergen with a new formulation and new application. We believe that this was one of the first stonemasonry companies in Australia to introduce the Integra adhesive from Canada; interestingly, a number of Canadian colleagues contacted had not seen any cases of ACD caused by this particular product. The manufacturers assured us that as the catalysed glue undergoes a rapid cross-linking polymerization reaction, there would be an insignificant amount of free unreacted MMA monomer remaining after it had passed through the static mixer. They did not believe that this could cause skin sensitization. However, the clinical evidence would suggest otherwise.

MMA is used in the production of many polymer-based products, including adhesives, acrylic glass, paints, inks, and dental and medical products (3). MMA adhesives have been used commercially for > 50 years (4), and classic applications have included plastic-to-plastic or plastic-to-metal bonding, for example affixing car bumpers. MMA adhesives have been used for some years by stone conservators (5); however, modified MMA adhesives have only recently gained popularity as bonding agents for quartz, natural stone, and porcelain products. Modified MMA adhesives offer many benefits, including

convenience, a rapid cure time, and high strength and colour stability (4, 6). Addition of an epoxy provides durability and resistance to high temperatures. According to the company's website, the Integra surface bonder also has greater bond strength than competitors, and provides the first colour-matched cartridge system designed specifically for the stone industry (7). The company suggests that the adhesive can be used on acrylic and polyester surfaces as well as on stone, that it provides invisible seams, and that it can be used for multiple applications involving dynamic loads (7).

Methacrylate monomers are strong sensitizers, and ACD caused by MMA in dental restorative materials, artificial nails, adhesives and orthopaedic cements is well described (8–10). Rarer sources of exposure include an insulin pump catheter, a microscope compounding resin, a leg prosthesis, and the poly(methyl methacrylate) component of gentamicin beads inserted for the treatment of local infection post-mastectomy (11–13). There is also a case report of ACD caused by an MMA-based cow hoof adhesive, which, like Integra, functions with a dual-compartment cartridge; however, according to the manufacturer's website, this contains polyurethane rather than epoxy (14). We could not find any reports of allergy to MMA in stonemasons or workers in similar industries, nor could we find any reports of allergy to MMA in an epoxy-modified MMA adhesive.

Although epoxy-based hardeners have been reported to cause ACD in marble workers (15, 16), neither of our patients reacted to epoxy resins or to the epoxy (meth)acrylate (bisphenol A-glycidyl methacrylate). Patch testing in both patients yielded a number of positive reactions to other methacrylates, indicating cross-reactivity. This is in keeping with animal studies, which have shown strong cross-reactivity between 2-HEMA, 2-HPMA, MMA, and EGDMA (17). It is also possible that other methacrylates were present in the adhesive as impurities or undeclared compounds.

These cases have important safety implications for workers in the stonemasonry industry and others using this new formulation of surface adhesive. Employers should be aware of the potential for sensitization, and enforce protective measures with the use of at least two pairs of disposable nitrile gloves. Dermatologists should remain alert for similar cases, and patch test relevant patients with acrylates.

References

- 1 Integra Adhesives. Material safety data sheet: Surface Bonder Xi, RPT-01, Trim Bonder TR30/TR40, Rodding Compound RD50, Sink Bonder SK11, 2012. Available at: <https://s3.amazonaws.com/media.integra-adhesives.com/web/products/acrylicadhesive-msds-na.pdf> (last accessed 09 March 2015).
- 2 Toholka R, Wang Y S, Tate B et al. The first Australian Baseline Series: recommendations for patch testing in suspected contact dermatitis. *Australas J Dermatol* 2014 Sep 7. doi: 10.1111/ajd.12186. [Epub ahead of print]
- 3 Kimber I, Pemberton M A. Assessment of the skin sensitising potency of the lower alkyl methacrylate esters. *Regul Toxicol Pharm* 2014; **70**: 24–36.
- 4 Briggs P C, Jialanella G L, Dillard D A. Advances in acrylic structural adhesives. In: *Advances in Structural Adhesive Bonding*, Dillard D A (ed): Cambridge, Woodhead Publishing, 2010; pp. 132–150.
- 5 Sacchi B, Giannini L, Frediani M et al. Methyl acrylate polymers as suitable materials for the conservation of stone: performance improvements through atom transfer radical polymerization. *J Coat Technol Res* 2013; **10**: 649–657.
- 6 Ebnesajjad S. Characteristics of adhesive materials. In: *Handbook of Adhesives and Surface Preparation*, 1st edition, Ebnesajjad S (ed): Oxford, William Andrew Publishing, 2011; pp. 137–183.
- 7 Integra Adhesives. Surface Bonder Xi technical data sheet, 2013. Available at: <https://s3.amazonaws.com/media.integra-adhesives.com/web/products/acrylicadhesive-techdata.pdf> (last accessed 09 March 2015).
- 8 Aalto-Korte K. Acrylic resins. In: *Kanerva's Occupational Dermatology*, Rustemeyer T, Elsner P, John S M et al. (eds): Berlin, Heidelberg, Springer-Verlag, 2012; pp. 543–558.
- 9 Kanerva L, Estlander T, Jolanki R et al. Occupational allergic contact dermatitis caused by exposure to acrylates during work with dental prostheses. *Contact Dermatitis* 1993; **28**: 268–275.
- 10 Mowad C M. Allergic contact dermatitis from acrylates in artificial nails. *Dermatitis* 2004; **15**: 51–53.
- 11 Saccabusi S, Boatto G, Asproni B et al. Sensitization to methyl methacrylate in the plastic catheter of an insulin pump infusion set. *Contact Dermatitis* 2001; **45**: 47–48.
- 12 Drucker A M, Pratt M D. Acrylate contact allergy: patient characteristics and evaluation of screening allergens. *Dermatitis* 2011; **22**: 98–101.
- 13 Fogo A, Bashir S, Higgins E M. Contact allergic dermatitis to methylmethacrylate in gentamicin beads used to treat a postmastectomy site infection. *Br J Dermatol* 2011; **165** (Supp. 1): 80.
- 14 McGrath E J, Darvay A, Lovell C R. Nail dystrophy and fingertip dermatitis as a manifestation of methyl methacrylate allergic contact dermatitis in a cow hoof trimmer. *Contact Dermatitis* 2009; **60**: 344–344.
- 15 Angelini G, Rigano L, Foti C et al. Occupational sensitization to epoxy resin and reactive diluents in marble workers. *Contact Dermatitis* 1996; **35**: 11–16.
- 16 Aalto-Korte K, Jungewelter S, Henriks-Eckerman M L et al. Contact allergy to epoxy (meth)acrylates. *Contact Dermatitis* 2009; **61**: 9–21.
- 17 Rustemeyer T, De Groot J, Von Blomberg B M E et al. Cross-reactivity patterns of contact-sensitizing methacrylates. *Toxicol Appl Pharmacol* 1998; **148**: 83–90.