

Allergic contact dermatitis from bisphenol A in PVC gloves

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Bisphenol A is used as an antioxidant in polyvinyl chloride (PVC) plastics and as an inhibitor of end polymerization in PVC. Since 1998, we have investigated 4 cases of contact allergy from bisphenol A in PVC gloves. Only the case of the first patient, a packer in the food industry, has been reported in detail. A dentist and an oral hygienist apprentice had used disposable PVC gloves made by the same manufacturer, both in 1999. The dentist's PVC gloves contained 0.044% bisphenol A. In 2002, a cabin servant had used 2 brands of household-type PVC gloves. Her gloves contained 0.12% and 0.07% bisphenol A. Moreover, 2 of the patients reacted to *p*-tertiary butyl catechol, a polymerization inhibitor in PVC, but the connection between the allergic reaction and the PVC gloves could not be proven. In 2002, we analysed 16 brands of disposable PVC gloves for medical use, covering at least 80% of the Finnish market. We found a very small amount of bisphenol A in 1 brand, and no *p*-tertiary butyl catechol in any of the gloves. Nowadays, it seems that manufacturers avoid using bisphenol A in the production of disposable gloves for medical use, but bisphenol A should be remembered as a possible contact allergen in PVC products.

Key words: chemical analysis; contact allergy; disposable gloves; occupational; *p*-tertiary butyl catechol; plasticizer. © Blackwell Munksgaard, 2003.

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Bisphenol A [2,2-bis(4-hydroxyphenyl)propane; INCI 4,4'-isopropylidene diphenol; 4,4'-(1-methylethylidene)bisphenol; CAS 80-05-7] is used as a monomer in the manufacture of polycarbonates and epoxy resins, as an antioxidant in polyvinyl chloride (PVC) plastics and as an inhibitor of end polymerization in PVC (1). It is also used in the production of epoxy di(meth)acrylates (vinyl ester resins) (2) and corrosion-resistant unsaturated polyester-styrene resins, as an antioxidant, a fungicide and an antimicrobial in cosmetics (3). The Product Register of the Chemicals Register in Finland (Finnish abbreviation KETU; http://www.sttv.fi/kemo/ture/product_register.htm) held by National Product Agency for Welfare and Health (Finnish abbreviation STTV) includes data on chemicals classified as dangerous or which may cause hazard. The Product Register contains data on more than 100 000 chemicals, of which around 30 000 are available in the market. A total of 97 preparations (in August 2003) contained bisphenol A. Most of the preparations were epoxy resin and phenol-formaldehyde resin.

Hardeners, and, interestingly, some brake fluids and anaerobic sealants, contained bisphenol A.

Sensitization from bisphenol A is rare. 2 of our 4 cases of allergic contact dermatitis from bisphenol A in vinyl gloves have been reported earlier (4, 5), but only the first one in detail (4). As far as we know, no other cases have been described. Besides PVC gloves, other sources of sensitization have been fibre glass (6), plastic shoes (7), semi-synthetic waxes (8), dental composite resin (9), denture material (10), the production of epoxy resins (11) and the manufacture of thermal recording paper (12).

Case Reports

Patient no. 1

Patient no. 1 has been reported earlier in detail (4).

Patient no. 2

Patient no. 2 was a 52-year-old dentist with a 3-year history of hand dermatitis. Her medical

history was negative for atopy. She had protected her hands with disposable gloves, mainly Evercare[®] vinyl gloves (Seleftrade AB, Spånga, Sweden) for 7 years. In spring 1999, she presented with eczema on the backs of her hands. Prick tests with standard environmental and dental care allergens were negative. Patch testing showed allergic reactions to bisphenol A (++), *p*-tertiary butyl catechol (+) and Merthiolate (+). Doubtful reactions were elicited by neomycin, bacitracin, 2,2-bis[4-(methacryloxy)phenyl]propane (bis-MA), gold sodium thiosulfate and Evercare[®] vinyl glove. The glove was tested in one test chamber (Finn Chamber[®], Epitest Oy, Tuusula, Finland) with a drop of water and in another with a drop of acetone. On chemical analysis in 1999, Evercare[®] vinyl gloves were found to contain 0.044% bisphenol A. Bis-MA was not detected. This case has been described in a congress abstract (5).

Patient no. 3

Patient no. 3 was a 23-year-old oral hygienist apprentice with a history of allergic rhinitis and childhood hand and foot dermatitis. After 2 years of training, she developed eczema on the backs of her hands. She had worn powdered vinyl gloves. The eczema healed during vacations. In spring 1999, examination showed glove-shaped eczema. On prick testing with common environmental allergens, she had positive reactions to hay and mugwort pollen, as well as to cat, dog and horse dander.

On patch testing, allergic reactions were elicited by *p*-phenylenediamine base (++), bisphenol A (++), *p*-tertiary butyl catechol (++), Evercare Soft[®] vinyl glove (+) and another brand of disposable vinyl glove (+). Pieces of the gloves were moistened with water and covered with Scanpor[®] tape (Norgesplaster A/S, Vennesla, Norway).

Patient no. 4

Patient no. 4 was a 51-year-old cabin servant on a passenger ship. She had had contact dermatitis from inexpensive jewellery and metal buttons. After 6 months of work, she developed eczema on her hands and forearms. She tried to use household-type vinyl gloves, but her eczema got worse. Her hand eczema healed when she started to use cotton gloves under the vinyl gloves. The eczema persisted on her forearms, where her skin was in direct contact with the vinyl glove. On patch testing in a local hospital, she had allergic ++ reactions to nickel sulfate, balsam of Peru and thiuram mix.

At the Finnish Institute of Occupational Health, on patch testing to relevant series and

her own products, she had allergic + reactions to tetraethylthiuram disulfide (TETD), bisphenol A, Swehand[®] Combex and Swehand[®] Combex-Light vinyl gloves (Softtouch AB, Göteborg, Sweden). The gloves were tested in 2 test chambers with water in one and acetone in the other. Prick tests with the common environmental allergens and natural rubber latex were negative.

In the second patch-test session 2 months later, allergic reactions were elicited by bisphenol A (++), TETD (+++), tetramethylthiuram monosulfide (+), Combex-Light vinyl glove with acetone (++) and with water (+), as well as by Combex vinyl glove with acetone (+) and water (+). Ultrasound extracts (13) of the 2 glove brands also gave allergic ++ reactions.

Chemical analysis determined that Combex vinyl glove contained 0.12% and Combex-Light vinyl glove 0.07% bisphenol A. 20 control patients tested negative on patch testing with Combex-Light and Combex vinyl gloves (tested in 2 chambers with acetone and water).

The patients' gloves were chemically analysed by a method that is described in the next paragraph.

Chemical Analyses of Bisphenol A, *p*-Tertiary Butyl Catechol and Plasticizer in Disposable PVC Gloves

16 brands of disposable PVC gloves for medical use (Table 1) were analysed for their bisphenol A, *p*-tertiary butyl catechol and plasticizer content in June 2002. The gloves covered at least 80% of the Finnish market. The chemical compounds were determined by gas chromatography with a mass selective detector and external standard method after extraction of the product samples with acetone. The extracted plasticizers were tentatively identified by comparing them to mass spectra in the Wiley library. The mass spectra of diethylhexyl phthalate and dioctyl phthalate (DOP) are very similar. We analysed all known plasticizers in soft PVC, which can be extracted by acetone and detected by gas chromatography.

The content of *p*-tertiary butyl catechol was below the detection limit (0.0005%) in all the vinyl gloves. The content of bisphenol A was below 0.001% in 15 brands of vinyl gloves, and 1 brand contained 0.005% bisphenol A. The analysed plasticizers are listed in Table 1.

Discussion

Polyvinyl chloride is made by polymerization of vinyl chloride monomer. Plasticizers, mainly phthalates, are added to PVC. Hard PVC contains approximately 10% and soft PVC up to

Table 1. Studied disposable vinyl gloves and plasticizers identified according to gas chromatography-mass spectroscopy results

Glove (product code)	Manufacturer	Plasticizer
SensiCare non-latex powdered medical examination gloves (14403L)	Maxxim Medical, Belgium	Diheptyl phthalate, dioctyl phthalate, diisononyl phthalate
SensiCare non-latex powder-free medical examination gloves (209V3F)	Maxxim Medical, Belgium	Diheptyl phthalate, dioctyl phthalate, dinonyl phthalate
Tru-Touch clear vinyl powdered medical examination gloves (SH2011849-2)	Maxxim Medical, China	Diisooctyl adipate, diethylhexyl phthalate
Tru-Touch PF vinyl powder-free (0900546-2)	Maxxim Medical, China	Diisooctyl adipate, diethylhexyl phthalate
Vinyl examination gloves powdered, TUV Product Service (000125)	SunMax Enterprise Shanghai, China	Diethylhexyl phthalate, diisononyl phthalate
Disposable powder-free vinyl gloves, TUV Product Service (011112)	SunMax Enterprise Shanghai, China	Diethylhexyl phthalate, diisononyl phthalate
Sempermed vinyl powder-free examination gloves (V2420571)	Semperit Technische Produkte, China	Diethylhexyl phthalate
Evercare [®] soft vinyl examination gloves, powder-free (0900893)	Selefatrade, Sweden	Diisooctyl adipate, diethylhexyl phthalate
Evercare [®] vinyl examination gloves, powder-free (2011134)	Selefatrade, Sweden	Diisooctyl adipate, diethylhexyl phthalate
Saila powdered vinyl glove, Suomen Sairaalatukku oy (011105)	SunMax Enterprise Shanghai, China	Diethylhexyl phthalate
Saila powder-free vinyl glove, Suomen Sairaalatukku oy (000720)	SunMax Enterprise Shanghai, China	Diethylhexyl phthalate
Arista pre-powdered vinyl examination gloves (060932)	Arista Latindo, Indonesia	Diisooctyl adipate, diethylhexyl phthalate
Arista powder-free vinyl examination gloves (010467)	Arista Latindo, Indonesia	Diisooctyl adipate, diethylhexyl phthalate
Evercare [®] soft powder-free and phthalate-free vinyl examination gloves	Selefatrade, Sweden	Alkylphenylether
Ulma-Nyl vinyl examination glove, non-sterile, lightly powdered (700148)	Ulma, Germany	Diethylhexyl phthalate
Sensisafe non-latex examination gloves, powder-free (AT2000112)	Laboratoires Euromedis, France	Diisooctyl adipate, diisooctyl phthalate, dinonyl phthalate (bisphenol A 0.005%)

60–70% plasticizers (14). Di(2-ethylhexyl)phthalate (DOP), butyl benzyl phthalate and di-*N*-butyl maleate are used as plasticizers for soft PVC (15). Sometimes, uncured epoxy resin is added as a plasticizer and stabiliser to PVC (16). Bisphenol A is used as an antioxidant in PVC plastics and as an inhibitor of end polymerization in PVC (1).

Contact allergy from PVC gloves is rare. The allergen responsible for the sensitization usually remains unknown (4). Organic pigment, Irgalite Orange F2G, was shown to be the causative agent in 1 case of contact eczema from PVC gloves of household type (16). A plasticizer, di(2-ethylhexyl) phthalate (DOP), caused a case of contact urticaria from the vinyl chloride slip guard of cotton gloves (17). The previously reported Patient no. 1 with bisphenol A allergy from PVC gloves had used household-type gloves and had glove-shaped dermatitis. She had also handled price-code labels and price-code ink. Chemical analyses showed bisphenol A in the PVC gloves, price code labels and price code ink (4).

Contact allergy to other PVC products is also relatively rare. Diphenylthiourea and its degradation product, phenylisocyanate, in PVC adhesive may elicit allergic contact dermatitis (18). Epoxy

resin in the PVC film used in patch testing caused allergic contact dermatitis in 13 patients (19). A pyridine derivative in PVC leather probably caused allergic contact dermatitis in 1 patient (20). Mercury chloride in PVC boots caused allergic contact dermatitis in 1 child (21).

Patient no. 2 had occupational allergic contact dermatitis from bisphenol A in disposable vinyl gloves. Bisphenol A was detected in her Evercare[®] gloves. At the same time, Patient no. 3 had used Evercare Soft[®] vinyl gloves made by the same manufacturer. Although no chemical analyses were carried out, the cause of her dermatitis was probably the bisphenol A in the gloves.

Interestingly, these 2 patients also reacted to *p*-tertiary butyl catechol, a polymerization inhibitor in PVC (22). Evercare Soft[®] and Evercare[®] gloves were analysed in spring 2002, but they did not contain bisphenol A or *p*-tertiary butyl catechol. Neither did Evercare[®] gloves from the year 1999 contain *p*-tertiary butyl catechol when analysed in 2002. Thus, the connection between sensitization to *p*-tertiary butyl catechol and the use of vinyl gloves could not be proven.

The bisphenol A content of vinyl gloves seems to vary at different times. Evercare[®] gloves

contained bisphenol A in 1999, but not in 2002. Bisphenol A in the production of PVC gloves can be replaced by other chemicals. In our present survey of the Finnish market, only 1 brand of disposable gloves contained a small amount of bisphenol A. Patient no. 4 had occupational allergic contact dermatitis from bisphenol A in her vinyl gloves of household type. Bisphenol A was detected in her gloves. Similarly, Patient no. 1 had used household-type vinyl gloves, and her gloves contained bisphenol A (4).

Bisphenol A is 1 possible allergen in PVC gloves, but its presence in PVC gloves is not uniform. When allergic contact dermatitis from PVC gloves is suspected, bisphenol A should be tested. Chemical analysis of the glove material is useful in confirming the diagnosis.

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