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PERMEABILITY OF SURGEONS' GLOVES TO METHYL METHACRYLATE

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The quick passage of methyl methacrylate at 21°C and 35°C through seven surgeon's glove materials in a diffusion chamber was quantified by gas-chromatographic analysis. Polystyrene-butadiene dissolved in methyl methacrylate, latex and polychlorobutadiene showed reversible expansion, during which material from the samples dissolved. In order to prevent these phenomena from interfering with the analyses, experiments were performed with 4.7 M methyl methacrylate in ethanol. Even then, the time in which methyl methacrylate permeated the membrane was too short for sufficient protection. When using these gloves, the orthopaedic surgeon who is fixing endoprostheses is no doubt occlusively exposed to methyl and other methacrylates, benzoyl peroxide, rubber additives, etc. Of glove materials which are not surgically used, vinyl was inferior to latex, whereas a very thin polyethylene copolymer did not change in methyl methacrylate, showed better resistance to diffusion, but was insufficiently elastic and easily perforated. A better protective material is urgently needed.

Key words: Latex; methyl methacrylate; permeability; polychlorobutadiene; polyethylene copolymer; polystyrene-butadiene; prostheses; surgeon's gloves; vinyl.

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Methyl methacrylate is used in orthopaedic surgery as a bone cement, particularly for fixation of hip and knee prostheses. Contact sensitizations to methyl methacrylate used in the operating theatre have been described, even sensory neuritis, affecting those parts of the hands most exposed to the acrylic cement. Recovery from the latter takes several months (Fisher 1979 and personal communication).

It is possible to distinguish several consecutive phases in the development of allergic contact dermatitis, viz. (1) induction, (2) clinical manifestation, (3) clinically silent sensitization with recurrences after unexpected exposure. Factors which play an important role in induction are: immunochemical properties of the contactant, concentration, vehicle, route, duration, extension and repetition of exposure, health and protection of the exposed skin, proneness of the exposed organism to respond to stimulation with the formation of T-effector and T-repressor cells. In view of these facts, we may all be regarded as on our way to become (contact) sensitized to one substance or another. Which substance will be "our" contact sensitizer depends on our pattern of life, resulting in a number of inevitable exposures. Whether such exposure has grave consequences depends on the possibility of replacing "our" contact allergen.

For an orthopaedic surgeon this means that he is on his way to develop contact sensitization to methyl methacrylate or other sensitizing components in the bone cement he uses, to rubber additives, etc. Nobody is able to detect how far he has already gone in the direction of sensitization, and how far he still has to go before sensitization becomes clinically apparent. The only way in which he may delay this disaster is to use a lower concentration, protect the skin, and keep it in good health.

The incidence of contact sensitization among orthopaedic surgeons at present is not of great importance, but the expected incidence is to be feared. Due to the phenomenon of group-specificity it is to be expected that an individual sensitized to methyl methacrylate will also react to quite a number of different acrylics (Van der Walle 1982), so that no allergen replacement is possible, and the surgeon must stop cementing endoprostheses. In addition, he will suffer from recurrences of his dermatitis as a result of exposure to acrylics used for various purposes in everyday life (Van der Walle 1982).

The incidence of contact sensitization to rubber chemicals is so high in the general population that some 16 of them have been incorporated in the screening series of contact allergens of the International Contact Dermatitis Research Group (Malten et al. 1976, Fregert 1974). The frequency with which allergen replacement is demanded by surgeons indicates that contact sensitization to these auxiliary substances is frequent among them, but in addition it can be rather serious if replacement is really impossible in certain cases. To our knowledge, exact statistics about this problem are not available.

It has been demonstrated that methyl methacrylate easily penetrates the usual rubber gloves, whereas in thick vinyl gloves permeation of methyl methacrylate could not be detected (Pegum & Medhurst 1971). To quantify these findings, we designed a test system in which we examined the permeability to methyl methacrylate of a collection of surgeon's gloves from our hospital, and of some gloves made of alternative materials.

MATERIAL AND METHODS

Chemicals. Methyl methacrylate (Merck-Schuchardt), ethanol (Merck p. A.), and butanone-2 (B.D.H.) contained no impurities interfering with the analysis. Neopentyl alcohol (Aldrich) and n-pentanol (B.D.H.) were fractionated before use.

Samples. We collected seven surgeon's gloves, three examination gloves, and a household glove (Table 1). Materials from the fingers were removed and tested by soaking in pure methyl methacrylate for 1 h, rinsing with fresh methyl methacrylate, then ethanol, and drying. Samples for permeation and density measurements were taken from the wrist; powder was removed by rinsing with alcohol, and the samples were dried.

Diffusion chamber. The chamber consisted of two square blocks of glass in which cylindrical apertures had been made, closed on one side with glass. Holes drilled in the blocks made it possible to screw them together, using screws furnished with rubber O-rings. Samples were placed vertically between flat rubber rings (from which soluble material had been removed by soaking in butanone-2 for several days and drying), fitting to the flat areas surrounding the cylindrical apertures. Both compartments of the chamber could be reached through glass-stoppered connections to holes drilled in the walls of the cylinders. The compartments could contain a volume of 5.75 ml; the available glove sample area was 3.14 cm^2. The contents of the compartments were stirred magnetically. The chamber was placed in a double-walled beaker. Water was pumped from a thermostat through the space in the wall. The beaker was covered with a sheet of foam plastic with holes for the glass-stoppered connections, and a controlling thermometer to regulate the temperature in the beaker. Experiments were performed at 21.0 ± 0.5°C, and 35.0 ± 0.5°C. Liquids were heated to these temperatures before introduction.

Analyses. Analyses were performed with a Hewlett Packard 402 gas-chromatograph with integrator 3373B, flame ionization detector and nitrogen carrier (2.5 cm^3 · min^{-1}) on a 6′ glass column containing 4.7% silicone OV 210 on Gaschrom Q. In an isotherm programme temperatures were: injection port 40°C, oven 43°C, detector 59°C. Mean retention times were: ethanol 50 s, neopentyl alcohol 125 s, methyl methacrylate 200 s, n-pentanol 285 s. In the solutions, neopentyl alcohol served as an internal standard to correct pipetting errors; n-pentanol had been added to prevent tailing of the methyl methacrylate peak.

Of standard solutions of methyl methacrylate in ethanol, containing 22.7 mM neopentyl alcohol and 22.7 mM n-pentanol, 1 µl samples were analysed. The errors were: 1 mM: 10% 2–5 mM: 3.5%, 6–150 mM: 1%, 160–600 mM: 4%. A calibration curve was obtained that differed slightly from linear.

In the diffusion chamber one compartment was filled with a blank solution: ethanol, containing 22.7 mM neopentyl alcohol, and 22.7 mM n-pentanol. The other was filled with 4.7 M (50% w/v) methyl mechacrylate in ethanol with the same additions. At the moment of

Table 1. Permeability of glove materials to methyl methacrylate

Glove material, colour	Density $g \cdot cm^{-3}$ (20°C)	Thickness mm	21°C Lag-time min	21°C $\mu mol \cdot min^{-1} \cdot cm^{-2}$	35°C Lag-time min	35°C $\mu mol \cdot min^{-1} \cdot cm^{-2}$
Perry X-Am Tex*						
latex	0.939	0.125	2	6.7	1.5	11.3
Seamless Sensi Grip White*						
latex	0.908	0.175	3.5	4.9	1.5	7.9
double layer			12	2.23		
Seamless Sensi Grip Brown*						
latex, brown	0.923	0.178	3.5	4.7	1.5	7.6
double layer					6	4.4
Seamless Brown Milled Regular*						
latex, brown	0.935	0.157	3	4.9	2.5	7.3
Travenol Triflex*						
latex	0.938	0.175	3.5	4.7	2	7.3
double layer					6.5	3.4
Elastyren*						
polystyrene-butadiene	0.952	0.156	1.5	8.2	1	18.3
Pioneer Rollpruf*						
polychlorobutadiene, green	1.26	0.145	4	5.1	2	9.5
Gyno-Daktarin Dispos-a-glove						
polyethylene copolymer	0.935	0.026	1.75	1.74	1	6.1
Parke-Davis Ready-Wrap						
vinyl, blue	1.16	0.111	<1	12.2	not determined	
Trutouch						
vinyl	1.17	0.155	1.5	10.1	not determined	
Marigold household						
latex, red	not determined		4.5	3.5	not determined	

*Sterilized surgeon's glove.

filling the latter compartment, a stopwatch and magnetic stirring were started. Eight to twelve 1 µl samples from the former compartment were analysed as a function of time within 90 min. Then the column was cleaned by heating to 250°C.

Used samples were rinsed with ethanol and dried. The analyses were performed in duplicate. With the exception of polystyrene-butadiene samples, the same sample was used a second time. Some glove materials were tested in double layers. In one glove, experiments were performed with material from both finger and wrist.

Density and thickness. At the sampling site a square area (23 × 23 mm) was stamped and cut out from each glove. The material was weighed, and the density determined with a pycnometer. From the data obtained the mean thickness of the material was calculated. The error in the latter was 3%.

Water permeability. We adapted our standard measurement of the water vapour loss from the skin (Malten & den Arend 1978) to estimate the water permeability of some of the materials before and after exposure to methyl methacrylate in the diffusion chamber. A measuring cup (area 1.875 cm^2) was pressed against the underside of the glove membrane. It was perfused with dry nitrogen as a carrier to bring the penetrating water to a modified Meeco moisture analyser. On top of the membrane an open glass cylinder was pressed, containing a 1.5 cm layer of water. The data were recorded after equilibrium was attained.

RESULTS

When the finger materials were soaked in methyl methacrylate, polystyrene-butadiene dissolved. Latex and polychlorobutadiene showed expansion, which reversed after removal of the methacrylate in which substances from the samples had dissolved to yellow-coloured solutions.

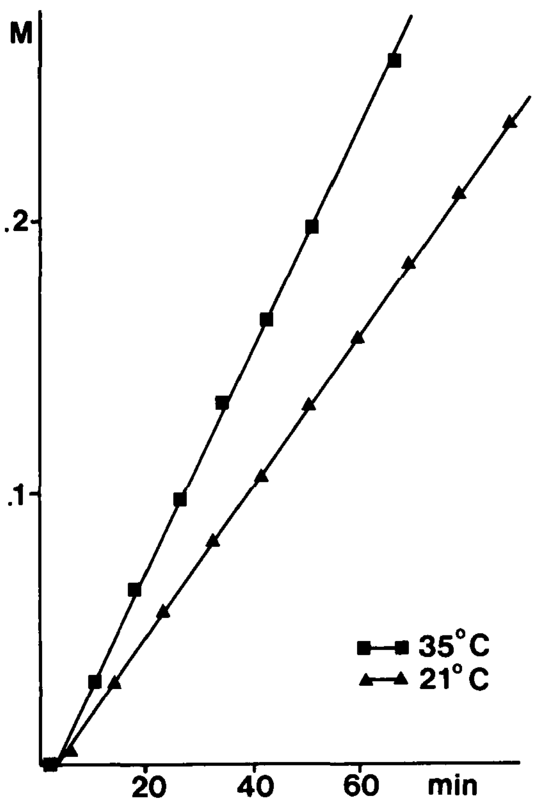

Figure 1. Permeability of surgeon's glove material (Seamless Brown Milled Regulator) to methyl methacrylate in a diffusion chamber. Concentration in acceptor compartment is shown as a function of time. Start concentration in donor compartment was 4.7 M in ethanol.

The least colour was extracted from polychlorobutadiene. After drying, non-dyed samples were visibly bleached. Except for Seamless Brown Milled Regular, five other latex samples showed a loss of stickiness, which was complete in those from Perry X-Am Tex and Seamless Sensi Grip White. In latex, no loss of elasticity was visible. In the two vinyl samples an initial expansion that decreased in the methacrylate was observed. After drying, these samples were harder and shrunken. The methacrylate remaining in the flask foamed and after evaporation of the monomer a syrup was left. No material could be extracted from polyethylene copolymer, which did not show any change.

The diffusion appeared to be a linear function of time for all glove materials except vinyl. In the latter samples a first rapid diffusion slowed down to 25% of its original rate after 90 min of exposure. After treatment with 4.7 M methyl methacrylate in ethanol, this material also appeared shrunken and harder at the end of experiments. Values for diffusion rates were obtained from the straight lines or, for vinyl, from the first points of measurement. Extrapolation of the lines obtained to zero concentration showed lag-times (Table 1), (Figure 1). Reproducibility of the results was good; deviations in duplicate experiments were less than 3%. Permeability at 35°C was substantially higher than that at 21°C; this difference was larger in synthetic polymers. Little permeability difference appeared in the various latex samples. The household glove had a rough surface, and measurement of its thickness would therefore not have been meaningful. Although this glove was made of considerably thicker latex than the surgeon's gloves, its permeability to methyl methacrylate was not much lower. Polystyrene-butadiene was ruptured during experiments in three out of four samples. In one experiment, performed with a sample from the finger of a surgeon's glove, an increase in thickness by 15% and a decrease in the diffusion rate by 25% appeared, as compared with the sample from the wrist.

Although repetition of the diffusion experiments with the same latex or polychlorobutadiene samples gave exactly the same results, the much more sensitive measurement of the water

Table 2. Permeability of surgeon's glove materials to water, before and after exposure to 4.7 M methyl methacrylate in ethanol, in $\mu g \cdot min^{-1} \cdot cm^{-2}$

Glove	Not exposed	Exposed
Perry X-Am Tex	3.6	3.0
Seamless Sensi Grip White	1.7	1.8
Seamless Sensi Grip Brown	1.8	1.2
Seamless Brown Milled Regular	2.0	1.1
Travenol Triflex	1.9	1.9
Elastyren	3.2	not determined
Pioneer Rollpruf	0.8	0.6

permeability revealed a decrease after exposure to methyl methacrylate in ethanol, except in two samples (Table 2).

DISCUSSION

In our diffusion experiments, aimed at quantitative comparison of glove materials, a 4.7 M solution of methyl methacrylate in ethanol had to be used to minimize expansion of the membranes and extraction of auxiliary substances, which would have interfered with the analyses.

While handing the so-called monomer-polymer adhesive mixture, the orthopaedic surgeon wears on top of his rubber gloves a pair of cotton gloves and on top of these another pair of rubber gloves. At the end of this phase of the operation, he removes the top rubber and cotton gloves and then continues with the remaining gloves. The exact composition of the adhesive mixture is still unknown, but the greater part of the acrylic monomer it supposedly contains is still methyl methacrylate. In addition, there must be (Malten 1982): a solvent, a starter (an amine or cobalt salt), a radical donor (benzoyl peroxide), an inhibitor (hydroquinone or a related substance), and possibly an antibiotic. The three last-mentioned chemicals are also known contact sensitizers (Lindemayr & Drobil 1981, Van der Walle et al. 1982).

The time needed for fixation of the prosthesis is generally much longer than the lag-time we found in our experiments, which is related to the time the methyl methacrylate needs to permeate the glove material. After removal of the outer gloves a considerable amount of monomer is left on and in the inner glove, as illustrated by our experiments with double layers. Taking into consideration the skin temperature of the surgeon, the measurements at 35°C are a better approximation of the real working circumstances than those at 21°C.

In the contact with the cement, low molecular-weight ingredients of the gloves dissolve in the monomer, especially from expanded parts. Among those are oligomers and auxiliary substances such as rubber additives.

In the manufacturing process the glove, after being formed, stays on the mould with the fingers down. The final flow of the very viscous material results in thicker latex in the fingers than in the wrist, in accordance with our observation, but also in thinner parts between the fingers. When the gloves are worn the contact is occlusive, which stimulates sensitization (Magnusson & Kligman 1970). Some materials showed a decrease in water permeability after exposure. This means that occlusion increases after contact with the monomer.

Elastyren gloves were developed especially for surgeons who are contact-allergic to certain rubber additives. These gloves contain only one additive, which has a very low allergenic potential (Hjorth 1972). In contact with the monomer, solution of this glove occurred in a short time. Pioneer Rollpruf is labelled "for those allergic to natural rubber" by the manufacturer. Natural rubber, however, does not induce contact sensitization (Cronin 1980). We have no information on its additives.

Considering the results of our investigation, there is no doubt that, when using these gloves, the surgeon is exposed to methacrylate under occlusion, but also to other contact-sensitizing chemicals such as benzoyl peroxide, hydroquinone, cobalt compound, rubber additives, antibiotics, etc.

Vinyl appeared to be an inferior material, releasing plasticizer in the monomer, and with the highest initial permeability. Polyethylene copolymer, although very thin, gave the best protection from methyl methacrylate diffusion. This material, however, is not sufficiently elastic, and is easily perforated by a sharp edge or a rough surface.

We must conclude that, during cementing of prostheses, protection is very unsatisfactory. Modern plastics technology should be able to produce a material that has the characteristics of polyethylene copolymer in the diffusion of methacrylate, but is thicker, mechanically stronger and somewhat more elastic, and does not contain sensitizing agents.

We tried to contact manufacturers of these materials but, even when the concern of occupational physicians in industries where similar problems exist and of dentists is added to ours, large-scale demands are improbable, and production is consequently not very interesting commercially.

More than ten years ago, Pegum & Medhurst (1971) reported the lack of protection in the use of rubber gloves. Nothing has been done to solve this problem. We hope that this paper may act as an eye-opener to the need to improve the quality of surgeons' gloves in terms of their permeability to the various materials handled.

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