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Resistance of Medical Gloves to Permeation by Methyl Methacrylate (MMA), Ethylene Glycol Dimethacrylate (EGDMA), and 1,4-Butanediol Dimethacrylate (1,4-BDMA)

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Gloves afford hand protection by minimizing skin contact. The effectiveness of medical gloves to protect against permeation of the monomers, methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), and 1,4-butanediol dimethacrylate (1,4-BDMA), was assessed focusing on permeation rates and degradation of glove materials caused by monomer contact. Fifteen different brands of gloves were tested using a European Standard procedure. Surface images of glove materials before and after exposure to the monomer mixture were obtained using a scanning electron microscope. The standard is not applicable as the only method for estimating the safety of gloves, but it is useful as guideline together with the cumulative permeation of acrylic monomers. Monomer contact on the outside resulted in substantial swelling of most glove materials, and structure changes of the inside surface.

permeation rate   degradation   breakthrough time   bone cement
adhesives   prosthetic materials

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1. INTRODUCTION

Professionals, in particular dental technicians processing dentures, crowns and bridges, dentists applying orthodontic appliances, and orthopedic surgeons handling bone cement, are at risk because they handle methyl methacrylate (MMA)-based products manually. Dental products may additionally contain cross-linking monomers like ethylene glycol dimethacrylate (EGDMA) and 1,4-butanediol dimethacrylate (1,4-BDMA; Ruyter & Øysæd, 1988). Polymerisation of mono- and dimethacrylate monomers is initiated chemically by mixing two components, or by light. Both ways require manual handling. Handling of MMA, EGDMA, and 1,4-BDMA requires protection because skin contact can cause allergies (Gebhardt & Geier, 1996; Geukens & Goossens, 2001; Kanerva et al., 2000; Kanerva, Estlander, & Jolanki, 1997; Kanerva, Estlander, Jolanki, & Hendricks-Eckerman, 1995; Kanerva, Jolanki, Leino, & Estlander, 1995; Kanerva, Lauerma, Estlander, & Alanko, 1996; Rustemeyer & Frosch, 1996; Wrangsö, Swartling, & Meding, 2001) and non-polymerized products most often cause allergies.

Health care personnel use gloves to prevent cross-contamination and to avoid skin contact with potentially hazardous substances. In dental clinics, medical gloves for single use are assumed to provide adequate protection. The effectiveness of a glove to protect against chemicals is based on resistance to degradation and permeation, and breakthrough time. The breakthrough times for MMA, EGDMA, and 1,4-BDMA through medical gloves is presented elsewhere (Lönnroth, Wellendorf, & Ruyter, in press). This paper focuses on permeation rate (the speed at which the monomers penetrate the glove materials), and degradation (the change in physical characteristics of the glove materials caused by contact with the monomers).

2. AIM

The aim of this study was to assess the applicability of calculating permeation rates using the rate equation in the European Standard No. EN 374-3:1994 (European Committee for Standardization [CEN], 1994) to estimate the safety of gloves. Additionally, to see if the inside surface of glove materials was affected by exposure to a monomer mixture of MMA, EGDMA, and 1,4-BDMA on the outside.

3. MATERIAL AND METHODS

Fifteen medical gloves, commonly used in Scandinavia, representing natural rubber latex (NRL) materials, synthetic rubbers, and synthetic polymeric materials, were selected for testing against permeation by MMA, EGDMA, and 1,4-BDMA. Additional tests were carried out using polyethylene film and double gloves (nitrile + NRL, and polyethylene + NRL). Data on the gloves is shown in Table 1. The test chemical consisted of MMA, EGDMA, and 1,4-BDMA in a mixture (see Table 2).

TABLE 1. Data on the Gloves Tested

Code	Name	Manufacturer	Type	Batch
Natural Rubber Latex Materials				
N1	Sempermed	Semperit, Austria	Latex + silicone inner coating	03971746x0007
N2	P&G Latex	Procter & Gamble, USA	Latex	804383
N3	Biogel™ D	Regent Medical, UK	Latex	97450
N4	Amanita	Athena Nordic, Sweden	Latex	3414
Synthetic Rubber Materials				
S1	Tactylon®	Tactyl Techn. Inc., USA	Styrene-ethylene--butadiene	7213-0002
S2	Elastyren®	ECI Medical Tech. Inc., Canada	Styrene-butadiene	96038
S3	Nitra Touch	Ansell Medical, UK	Nitrile rubber	8020311012
S4	Nitril	Opti Pappers Gruppen AB, Sweden	Nitrile rubber	90728003
S5	N-Dex Nitrile	Best Manufacturing Co, USA	Nitrile rubber	A98027B
S6	Lirtin	Seleftrade AB, Sweden	Nitrile rubber	90928009
Synthetic Polymeric Materials				
PE	PE film	No information	Polyethylene	no information
P1	Metin	Medical Technology, Norway	Polyvinyl chloride	0001/9741
P2	Sensicare	Maxxim Medical Inc., USA.	Polyvinyl chloride	701M3F
P3	Evercare	Seleftrade AB, Sweden	Polyvinyl chloride	2015
P4	Glads vinyl	Tena, Sweden	Polyvinyl chloride	960926
P5	Examination gloves	Opti Pappers Gruppen AB, Sweden	Polyethylene, annealed	no information

Circular samples, with a diameter of 10 cm, were cut from the palm of the gloves. Thickness of materials was measured at 5 points, 1 central and 4 peripheral, using a micrometer (Mitutoyo, Japan). Mean and *SD* were calculated for each material.

TABLE 2. Data on the Mono- and Dimethacrylate Monomers Tested

Names of Monomers (Test Mixtures)	Proportion (%)	CAS	Molecule Mass	Batch No.	Manufacturer
MMA (methyl methacrylate)	80	80-62-6	100.1	283302688	Fluka (Buchs, Switzerland)
EGDMA (ethyleneglycol dimethacrylate)	10	97-90-5	198.2	854390	Merck-Schuchardt (Hohenbrunn, Germany)
1,4-BDMA (1,4-butanediol dimethacrylate)	10	2082-81-7	226.3	7241970	Merck-Schuchardt (Hohenbrunn, Germany)

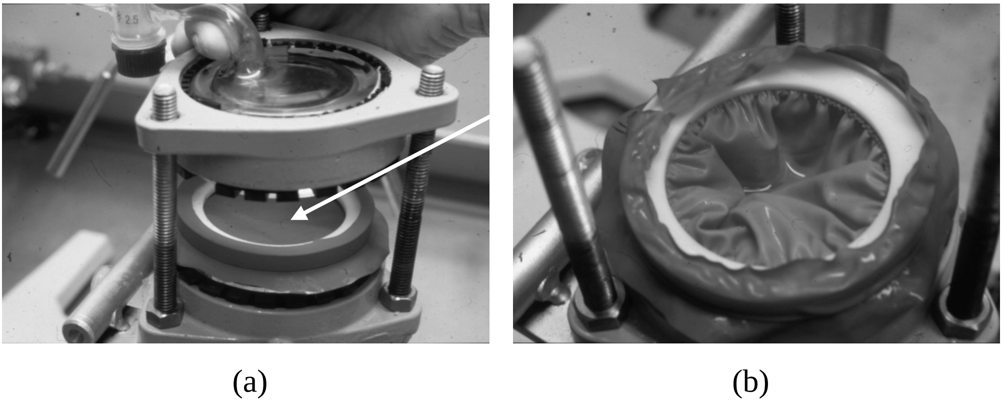
Testing was carried out according to the European Standard No. EN 374-3:1994 (CEN, 1994). The test apparatus consisted of a two-compartment cell with the glove material placed between the two halves. Distilled water was added into the compartment as a collecting medium (on the glove's inside). A stirring rod placed in the collecting medium allowed continuous mixing. The other compartment was completely filled with the test chemical (on the glove's outside), and the time of monitoring started. The exposed membrane area was 21.24 cm^2. Samples of 1 ml were taken from the collecting medium after the maximum of 2 hrs. Each sample was replaced with distilled water.

High-performance liquid chromatography (HPLC) was applied to determine the concentration of monomers in the samples. The chromatographic system consisted of two pumps, Model 2150, a controller, Model 2152, and a diode array detector, Model 2140 (LKB-Produkter AB, Sweden). The system was equipped with a 5-µm ChromSpher C-18 column (Chrompack, The Netherlands). The components were separated by isocratic elution with 70% CH_3CN and 30% H_2O. The flow rate was 0.8 ml/min and detection was performed at 205 nm for low concentrations and 225 nm for high concentrations. For the quantitative determination of monomers, standard calibration curves were obtained by plotting peak areas of known concentrations of the respective monomers. Breakthrough time (BTT, min) was recorded as the time when the analytic equipment detected a permeation rate of 1μg min^{-1} cm^{-2} (*P* value). The time for maximum permeation rate was identified, and cumulative monomer transfer/cm^2 at the end of the test was calculated. All tests were repeated twice if BTTs obtained were within ±20% (according to the requirements in the standard). If not, the tests were repeated.

Surface images up to 200× magnification of the inner surface of glove materials, before and after exposure to monomer mixture on the outside, were obtained using a scanning electron microscope (SEM, Philips XL 30 D643, The Netherlands) in order to see if changes in the materials could be observed.

4. RESULTS

All glove materials (except polyethylene) expanded substantially during the experiments, in particular natural rubber and nitrile rubber materials (see Figure 1). Within each batch of glove material, the thicker material had a lower MMA transfer at the end of the test, and a lower maximum permeation rate, compared to thinner materials, except for the nitrile rubber materials S3 and S4. The transfer of EGDMA and 1,4-BDMA was lower through all gloves compared to the transfer of MMA, a correlation between thickness of glove materials and permeation rate was not observed.



(a) (b)

Figure 1. A nitrile rubber glove (S4) before testing (a) and the same material immediately after 30-min exposure to the monomer mixture (b).

The permeation curves showed a rapid permeation of MMA through most gloves, with lowest permeation through the polyethylene glove P5, followed by the nitrile rubber S3, and the styrene-ethylene-butadiene glove S1 (see

Figure 2). Significantly lower amounts of MMA had permeated through the polyethylene compared to the other gloves at the end of the test. The nitrile rubber glove S3 had low permeation in the beginning but permeation increased rapidly after 30 min and reached the same level as the other gloves at the end of the test (Figure 2).

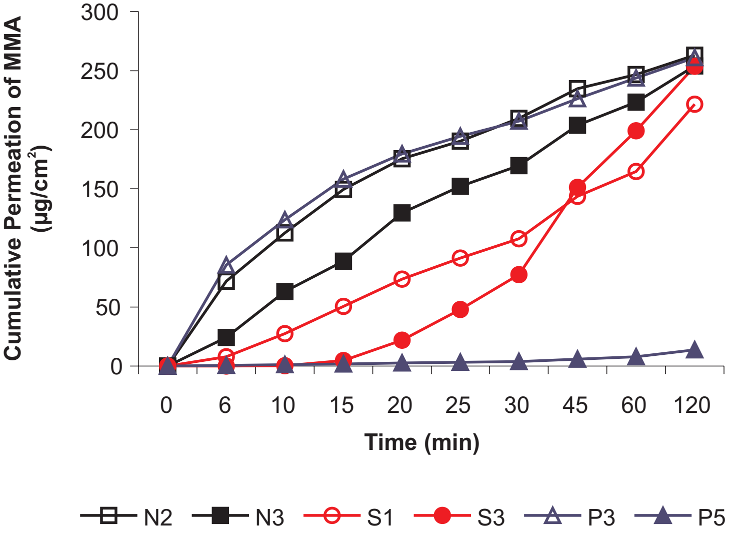


Figure 2. Cumulative permeation of methyl methacrylate (MMA) through two nitrile rubber materials (N2 and N3), two synthetic rubber materials (S1 and S3), and two synthetic polymeric materials (P3 and P5).

The polyethylene glove (P5) showed the best resistance to permeation in this study. However, the glove material was annealed and thus thinner than measured. To assess a polyethylene material without texture, a polyethylene film (PE; thickness 20 µm, *s* ± 0) was tested. The breakthrough time for MMA was 2 min through P5 and 2–10 min through the PE film. Breakthrough time could not be determined for EGDMA through P5 and PE. The breakthrough time for 1,4-BDMA was 25 min through P5 in one of three tests, and could not be determined in the other two, or through the PE film. However, EGDMA and 1,4-BDMA permeated slowly through both the P5 glove and the PE film, and could be quantified (Figure 3).

Testing double gloves with a nitrile rubber inner glove and a natural rubber outer glove was not possible due to the swelling of both materials. However, testing could be carried out after rinsing one material in water before putting them together in the test apparatus. The results should significantly lower permeation rates for monomers with a wet interphase, as shown for MMA in Figure 4.

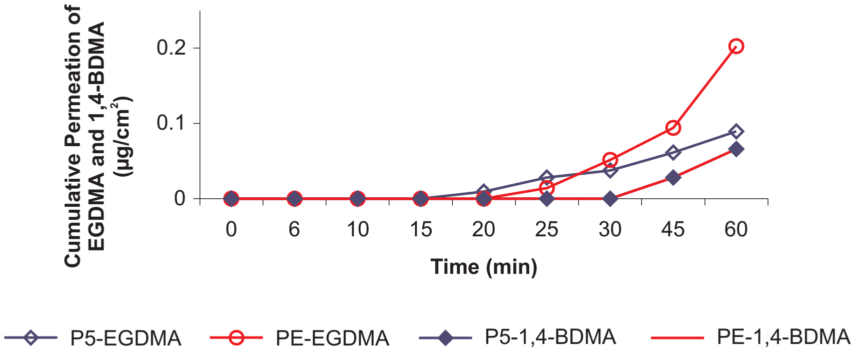


Figure 3. Cumulative permeation of EGDMA and 1,4-BDMA through two polyethylene materials (P5 and PE).

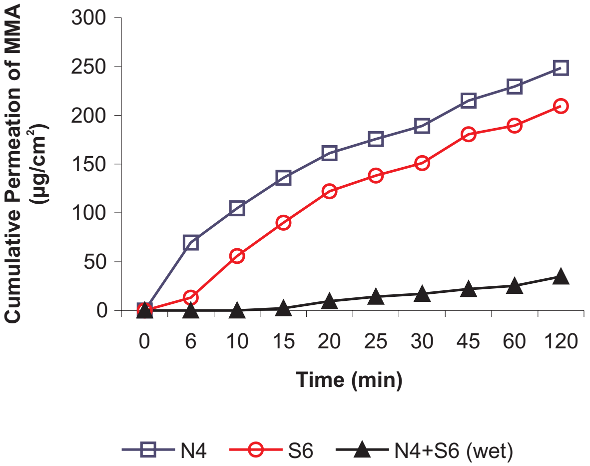
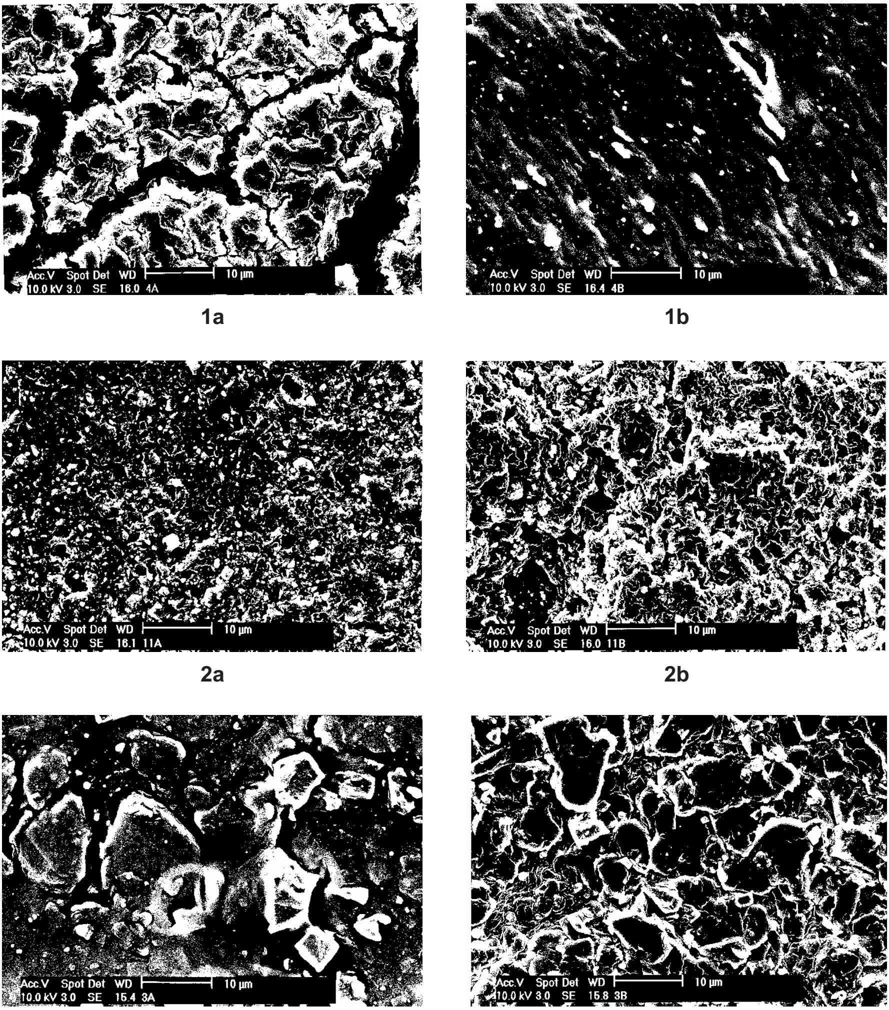


Figure 4. Cumulative permeation of MMA through a natural rubber glove (N4) and a synthetic rubber glove (S6) separately, and with both materials together + a wet interphase (N4 + S6).

SEM images showed that inside surfaces of most glove materials were affected after 30-min contact with the monomer mixture on the outside. Figure 5 shows inside surfaces of one nitrile rubber, one polyvinyl chloride, and one natural rubber material before monomer exposure (a) and after monomer exposure (b).



1a 1b

2a 2b

3a 3b

Figure 5. Inside surface of a natural rubber material (1), a synthetic rubber material (2), and a synthetic polymeric material (3) before exposure to the monomer mixture on the outside (a) and after 30-min exposure to the monomer mixture on the outside (b).

5. DISCUSSION

Using breakthrough time as a measure of protection and comparing materials is not sufficient, as shown in this study. Permeation of EGDMA and 1,4-BDMA could be quantified through the polyethylene glove and the polyethylene film, but BTTs could not be determined due to low permeation curves. Thus, BTT cannot be seen as a safe limit to a sensitized person.

Changes in glove materials, caused by contact with the monomer mixture, appeared as swelling of most materials, but also fragmenting and dissolving was observed. Swelling results in a larger surface area and thus a higher permeation of monomers. Due to the irregular shape of the expanded material and the continuous changing of shape and area it was not possible to measure the area in the closed system. Thus, calculations of the permeation rates were made on the basis of permeated monomers per initial exposed surface area.

Most swelling was observed in nitrile rubbers and natural rubbers probably because these materials are more polar, whereas polyethylene is nonpolar and thus not affected by monomer contact. Fragmenting of the Metin glove (polyvinyl chloride) and dissolving of Tactylon® (styrene-butadiene) may depend on low cross-linking density and a type of cross-linking. Metin glove material did not fragment when tested with a mixture using only EGDMA and 1,4-BDMA (Lönnroth et al., in press). This indicates that the degradation was caused mainly by MMA.

Glove materials with initial microscopic holes were easily detected due to the observed high quantities of the monomers in the aquatic medium. Such experiments were excluded and repeated. This was the case for one natural rubber latex material (P&G latex), which was tested 6 times because three samples had microscopic holes resulting in initial high quantities of the monomers in the aquatic medium. Additional water leakage tests according to the EN standard (CEN, 1994) for a leakage test showed no leakage.

The SEM images showed substantial differences in the appearance of the inner surface after the glove material had been permeated by the monomers. This phenomenon is probably due to degradation of glove materials. Degradation of glove materials after monomer contact is important because the gloves do not provide expected protection. Further, degradation may also enhance permeation of viruses as shown earlier by Rickards, Sydiskis, Davidson, Josell, and Lavine (1993) for NRL gloves treated with chloroform and acrylic monomers, and by Klein, Party, and Gershey (1990) for vinyl gloves treated with 70% ethanol.

It is well known that laminated systems with different layers have higher resistance to diffusion and permeation when the layers have different polarity properties. In this case water acted as the polar layer between the two glove layers resulting in significantly longer resistance to permeation.

6. CONCLUSION

None of the medical gloves tested provided enough protection against permeation by the monomer mixture in this study. The standard is not applicable as the only method for estimating the safety of gloves, but it is useful as a guideline together with the cumulative permeation of acrylic monomers. Exposure to the monomer mixture resulted in degradation of most glove materials. Polyethylene materials may give good protection when handling mixtures containing MMA but it is important to choose a material without texture because textured materials have lower strength resulting in lower protection. Additionally, the fit, comfort, and feeling are much lower in polyethylene gloves. Development of new medical gloves with good protection, fit, comfort, and feeling is needed.

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