

Permeability of Medical Gloves to Mono- and Dimethacrylate Monomers in Dental Restorative Materials

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Dental personnel manually handle methacrylate-based restorative materials, which can cause skin irritation and allergies. The protection given by different types of medical gloves is not well known. Breakthrough time (BTT, min) was used as a measure of protection according to a European standard, using 2 test mixtures consisting of respectively 3 and 5 monomers. Fourteen gloves representing natural rubber latex, synthetic rubber, and synthetic polymeric material were tested. The BTT ranged from some minutes to more than 2 hrs for the 4 monomers with a molecular mass less than 300. The longest protection was recorded for Nitra Touch (nitrile rubber), Tactylon (synthetic rubber), and Metin (PVC).

protection methacrylates composites resins adhesives

1. INTRODUCTION

Dental composites, resin-based crown and bridge materials, dental adhesives, and bonding materials contain mono- and dimethacrylates. Triethyleneglycol

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dimethacrylate (TEGDMA) and urethane dimethacrylate (UEDMA) are common monomers in resin-based crown and bridge materials. Some resin systems are also based on bisphenol-A dimethacrylate (BIS-GMA; Ruyter & Sjøvik Kleven, 1987). The monomers TEGDMA, UEDMA, and BIS-GMA are also components in composite resins (Ruyter & Øysæd, 1988). Dental composite materials often contain TEGDMA, BIS-GMA, and ethoxylated bisphenol-A dimethacrylate (BIS-EMA; Ruyter, 1982; Ruyter & Øysæd, 1987; Ruyter & Sjøvik, 1981). The main monomer in many dentin-bonding agents and light cured glass-ionomers is 2-hydroxyethyl methacrylate (2-HEMA; Ruyter, 1995). Visible light cured materials contain a photo initiator and a reducing agent like 2-(N, N-dimethylamino) ethyl methacrylate (Ruyter, 1982; Ruyter & Øysæd, 1988). Common additives in dental materials are 2-methoxyethyl methacrylate, used in bonding agents, and 4-methacryloxyethyl trimellitic anhydride (4-META), used in dental resins. Both monomers are added in order to promote adhesion.

Contact with acrylate and methacrylate (acrylic) monomers have been reported to cause skin symptoms and induce allergies (Jolanki, Kanerva, & Estlander, 1996, 1995; Kanerva, Estlander, & Jolanki, 1997; Kanerva, Estlander, Jolanki, & Henriks-Eckerman, 1995a; Kanerva, Jolanki, Leino, & Estlander, 1995b; Kanerva, Lauerma, Estlander, & Alanko, 1996; Kanerva, Mikola, Henriks-Eckerman, Jolanki, & Estlander, 1998; Pirila et al., 1998, Savonius, Keskinen, Tupparainen, & Kanerva, 1993). Dental personnel are at risk when handling acrylic monomers manually in their profession. Several studies have indicated that the prevalence of skin symptoms among dental personnel is high (Burke, Wilson, & Cheung, 1995; Hill, Grimwood, Hermes, & Marks, 1998; Jacobsen, Derand, & Hensten-Pettersen, 1996; Lönnroth & Shahnava, 1998a, 1998b, 1998c; Munksgaard, Hansen, Engen, & Holm, 1996; Mürer, Poulsen, Roed-Petersen, & Tüchsen, 1995; Rustemeyer & Frosch, 1996; Uveges, Grimwood, Slawsky, & Marks, 1995).

Dental personnel considered handling acrylic monomers to be hazardous, according to Lönnroth and Shahnava (1998a). Most of them used natural rubber latex gloves or poly (vinyl chloride) gloves as protection, and less than 2% used gloves of alternative materials (Lönnroth & Shahnava 1998b). There are a number of alternative glove materials available such as butyl rubber, chloroprene rubber, fluor rubber, nitrile rubber, styrene-butadiene rubber, and styrene-ethylene-butadiene rubber, and other compositions of synthetic polymer materials like ethylene-methyl-acrylate (EMA) or polyethylene (PE; Mellström, Wrangsjö, Wahlberg, & Fryklund, 1996). Little is

known about the resistance to permeation by monomers through different glove materials.

2. AIM

The purpose of this study was to determine the breakthrough time (BTT, min), as a measure of protection, against permeation by 2-hydroxyethyl methacrylate (2-HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A dimethacrylate (BIS-GMA), ethoxylated bisphenol-A dimethacrylate (BIS-EMA), urethane dimethacrylate (UEDMA), 2-methoxyethyl methacrylate, 2-(N, N-dimethylamino) ethyl methacrylate, and 4-methacryloxyethyl trimellitic anhydride (4-META) through medical gloves representing natural rubbers, synthetic rubbers, and synthetic polymeric materials.

3. METHOD

Fourteen different brands of non-powdered protective gloves were tested, 4 represented natural rubber latex (NRL), 6 synthetic rubber materials, and 4 represented synthetic polymer materials. All glove materials were tested using two monomer mixtures. Test mixture 1 represents a standard dentin, adhesive, or bonding mixture consisting of 2-HEMA, TEGDMA, and BIS-GMA (proportion 30:40:30). Test mixture 2 represents a corresponding dentin, adhesive, or bonding mixture consisting of BIS-EMA, UEDMA, 2-methoxyethyl methacrylate, 2-(N, N-dimethylamino) ethyl methacrylate, and 4-META (proportion 30:30:30:5:5; see Tables 1 and 2).

Circular samples, with a diameter of about 10 cm, were cut from the palm of each glove. Thickness of material was measured according to Standard No. ISO 4648:1991 (International Organization for Standardization [ISO], 1991) at 5 points, 1 central and 4 peripheral, using a micrometer (Mitutoyo, Japan). Mean and standard deviation were calculated for each material.

Testing was carried out in a ventilation hood at 20 ± 1 °C, and according to the European Standard No. EN-374-3:1994 (European Committee for Standardization, 1994). The test apparatus consisted of a two-compartment cell with the glove material placed between the two halves of the permeation cell for contacting the test chemical on the glove's normal outside surface, and the collecting medium on the glove's normal inside surface, see Figure 1.

TABLE 1. Data on the Gloves Tested

Code	Name	Manufacturer	Type	Thickness (μm)	Batch
Natural Rubber Materials					
N1	P&G Latex	Proctor & Gamble, USA	Latex	144.5 \pm 6.4	804383
N2	Sempermed	Semperit, Austria	Latex + silicone inner coating	155.5 \pm 11.7	03971746x0007
N3	Amanita	Athena Nordic, Sweden	Latex	159.0 \pm 7.0	3414
N4	Biogel™ D	Regent Medical, UK	Latex	246.0 \pm 8.8	97450
Synthetic Rubber Materials					
S1	N-Dex Nitrile	Best Manufacturing Co., USA	Nitrile rubber	95.5 \pm 8.3	A98027B
S2	Lirtin	Selefrade AB, Sweden	Nitrile rubber	110.5 \pm 7.6	90928009
S3	Nitril	Opti Pappers Gruppen AB, Sweden	Nitrile rubber	119.5 \pm 7.2	90728003
S4	Nitra Touch	Ansell Medical, UK	Nitrile rubber	136.5 \pm 4.1	8020311012
SB	Elastyren®	ECL Medical Tech. Inc., Canada	Styrene-butadiene	222.5 \pm 11.8	96038
SEB	Tactylon®	Tactyl Techn. Inc., USA	Styrene-ethylene-butadiene	224.0 \pm 18.2	7213-0002
Synthetic Polymeric Materials					
P1	Glads vinyl	Tena, Sweden	Poly (vinyl chloride)	89.0 \pm 5.7	960926
P2	Sensicare	Maxxim Medical Inc., USA.	Poly (vinyl chloride)	131.5 \pm 6.7	701M3F
P3	Evercare	Selefrade AB, Sweden	Poly (vinyl chloride)	162.0 \pm 21.9	2015
P4	Metin	Medical Technology, Norway	Poly (vinyl chloride)	194.0 \pm 51.9	0001/9741

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

Names of Monomers	Proportion (%)	CAS	Molecule Mass	Batch	Manufacturer
<i>Test mixture 1</i>					
2-HEMA (2-hydroxyethyl methacrylate)	30	868-77-9	130.1	364398/1	Fluka
TEGDMA (triethyleneglycol dimethacrylate)	40	109-16-0	286.3	350289/1	Fluka
BIS-GMA (Bisphenol-A dimethacrylate)	30	1565-94-2	512.0	73425	Sci-Pharm
<i>Test mixture 2</i>					
2-methoxyethyl methacrylate	30	6976-93-8	144.2	92818	Polysciences
2-(N,N-dimethylamino)ethyl methacrylate	5	2867-47-2	157.2	2-2218	Polysciences
4-META (4-methacryloxyethyl trimellitic anhydride)	5	70293-55-9	304.2	43328	Polysciences
BIS-EMA (Ethoxylated Bisphenol-A dimethacrylate)	30	24448-20-2	452.0	26999	Polysciences
UEDMA (Urethane dimethacrylate)	30	72869-86-4	471.0	819520	Vivadent Schaan

The exposed membrane area was 21.24 cm². A volume of 80 ml 0.1% Triton X100 (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) in water grade 2, Standard No. ISO 3696:1987 (ISO, 1987) was added into the compartment as a collecting medium (on the material's normal inside surface). A stirring rod was placed in the collecting medium to allow continuous mixing. The other compartment was completely filled with the test chemical (on the material's normal outside surface), and time of monitoring started. Test samples of 1 ml were taken from the collecting medium after 0.5, 1, 2, 3, 6, 10, 15, 20, 25, 30, 45, 60, 75, 90, 105, and 120 min, and each sample was replaced with 1 ml 0.1% Triton X100 (a non-ionic detergent) solution.

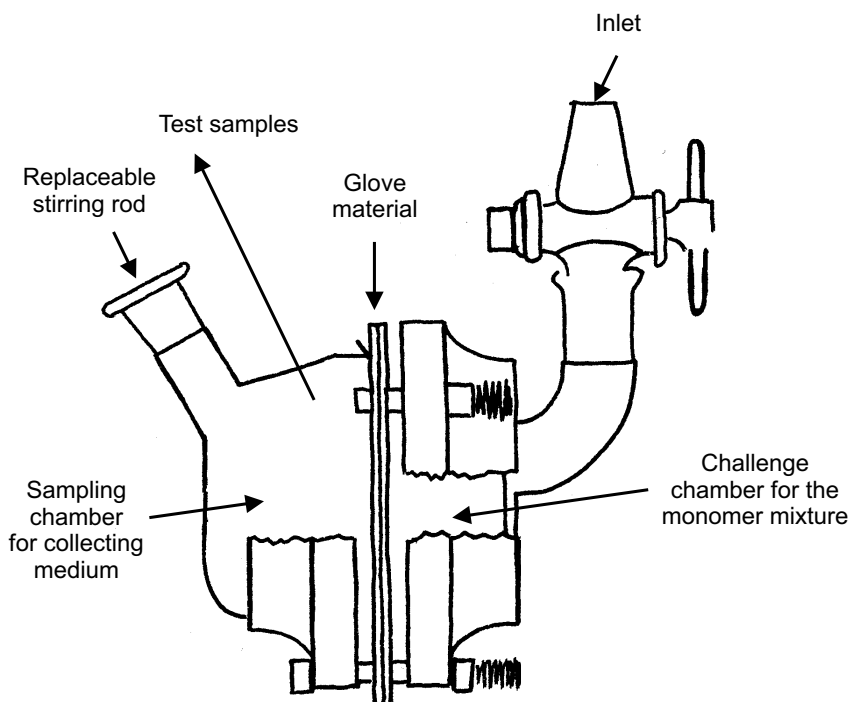


Figure 1. A schematic drawing of the test apparatus.

To determine the concentration of monomers in the sampled liquids, high-performance liquid chromatography (HPLC) was applied. The chromatographic system consisted of two pumps, Model 2150, a controller, Model 2152, and a diode array detector, Model 2140 (LKB-Produkter AB, Bromma, Sweden). The system was equipped with a 5- μ m ChromSpher C-18 column (Chrompack, The Netherlands). The components were separated by isocratic elution with 70% CH₃CN and 30% H₂O. The flow rate was 0.8 ml/min and

detection was performed at 205 nm for low concentrations and 225 nm for high concentration. For the quantitative determination of monomers, standard calibration curves were obtained by plotting peak areas of known concentrations of the respective monomers.

The collecting medium was analyzed quantitatively for the monomers and thereby the quantity that permeated the barrier as a function of time after its initial contact with the glove material. Breakthrough time, (BTT, min) was recorded as the time when a permeation rate of $1\mu\text{g min}^{-1}\text{ cm}^2$ (P value) was obtained. The quantity of a monomer that permeated the glove material from the initial contact with the glove material was calculated as a function of time and area according to

$$P = (C_i - C_{i-1} (V_t - V_s/V_t)) V_t / (t_i - t_{i-1}) A,$$

where P —permeation rate, $\mu\text{g min}^{-1}\text{ cm}^{-2}$; i —an index number assigned to each discrete sample, starting with $i = 1$ for the first sample; t_i —the time at which the discrete sample i was removed, in minutes; C_i —the concentration of the chemical in collecting medium at time t_i in micrograms per liter; A —area of the glove material in contact, in cm^{-2} ; V_t —total volume of the collection medium in liters; V_s —volume of the discrete sample removed from the collecting medium in liters.

The collecting water was analyzed prior to each experiment in order to detect monomer contamination of the equipment from the previous experiment. The tests were repeated twice, if the results obtained were the same. If not, tests were repeated until two similar results were obtained, in a few cases up to 4 times. The BTTs are presented with minimum and maximum values for each glove material and for each monomer.

4. RESULTS

Small quantities of BIS-EMA, BIS-GMA, and UEDMA could be detected after about 60 min through some gloves, but BTTs could not be determined through any of the gloves during the test period, due to low permeation rate. 4-META could only be determined through the natural rubber glove Amanita (N3) after 20 min in one test and 25 min in the other. Table 3 shows the minimum and maximum BTT values for the eight monomers tested.

TABLE 3. The Shortest and Longest Breakthrough Times (in min) for Mono- and Dimethacrylate Monomers, Based on 2-4 Experiments and 2-hr Testing. The Materials in Each Group Are Coded With 4 as the Thickest Material, and a Subgroup (S1-S4) Representing Nitrile Rubbers

Glove Code	Test Mixture 1				Text Mixture 2			
	2-HEMA	TEGDMA	BIS-GMA	2-methoxyethyl methacrylate	2 (N,N-dimethyl amino) ethyl methacrylate	4-META	BIS-EMA	UEDMA
<i>Natural rubber latex (NRL) materials</i>								
N1	15-25	6-20	>120	3	60-75	>120	>120	>120
N2	20	60-90	>120	3	30-75	>120	>120	>120
N3	15	10-15	>120	20-25	10-15	2-25	>120	>120
N4	45-105	20-25	>120	6-10	105->120	>120	>120	>120
<i>Synthetic rubber materials</i>								
S1	10-30	30-60	>120	6	45-75	>120	>120	>120
S2	60->120	60->120	>120	75->120	>120	>120	>120	>120
S3	45-60	75-90	>120	20-45	45-90	>120	>120	>120
S4	>120	>120	>120	90->120	>120	>120	>120	>120
SB	25-75	20-30	>120	6	45->120	>120	>120	>120
SEB	>120	>120	>120	6	60-75	>120	>120	>120
<i>Synthetic polymeric materials</i>								
P1	15	15-20	>120	3-6	3-6	>120	>120	>120
P2	10	15	>120	2-3	2-3	>120	>120	>120
P3	25-30	45	>120	6-10	6-10	>120	>120	>120
P4	105->120	105->120	>120	10-25	60-75	>120	>120	>120

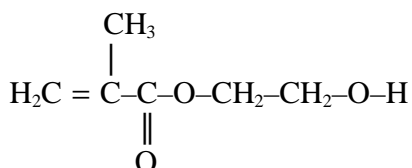
According to Table 3, the smaller monomer molecule 2-HEMA permeated earlier than TEGDMA through most gloves, except through the natural rubber gloves P&G latex (N1), Sempermed (N2), and Amanita (N3), and the styrene-butadiene glove Elastyrene® (SB). The thickest material in each group (N4, S4, and P4) resisted permeation by the monomers longest, except for Lirtin (S2) which resisted permeation by 2-(N, N-dimethylamino) ethyl methacrylate as long as Nitra Touch (S4).

The P&G latex glove material (N1), had to be tested four times because results differed widely. Additional water and air leakage tests of the glove material did not indicate micro-punctures.

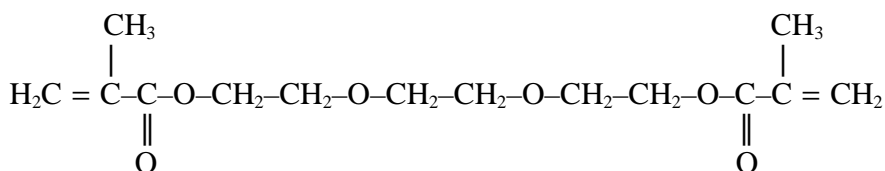
5. DISCUSSION

The structure and size (molecule mass) of the monomer influence the permeability, as shown in a previous study by Lönnroth, Wellendorf, and Ruyter (2002). An aromatic structure or a large molecular mass (304.2–512) explain why BTTs could not be determined for BIS-EMA, BIS-GMA, UEDMA, and 4-META through most of the gloves. The fact that 4-META permeated only through Amanita (N3) during the test period is remarkable and difficult to explain. TEGDMA is larger than that of 2-HEMA, see molecular structure below, but TEGDMA permeated earlier than 2-HEMA through 3 out of 4 natural rubber gloves, which might be explained by polarity of the monomers and glove materials. The slightly larger molecule 2-methoxyethyl methacrylate permeated much earlier than 2-HEMA through many gloves, which also might be explained by polarity phenomena.

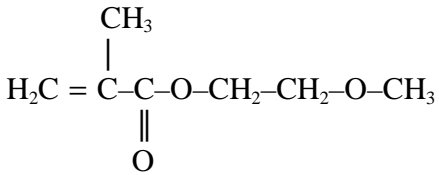
2-HEMA



TEGDMA



2-methoxyethyl methacrylate



Munksgaard (1992) reported that Elastyrene® burst after 50-min contact with a mixture of 2-HEMA, TEGDMA, BIS-GMA, and UEDMA (25 w/w-% of each). In this study, the Elastyrene® glove resisted permeation by the monomers longer than most natural rubber and synthetic polymer gloves, and did not burst during 2 hrs of testing with any of the mixtures, maybe because no stress was applied to the material and only minor swelling effects were observed. Another explanation could be improvements of the material like cross-linking, or that the test mixture used by Munksgaard had a higher temperature. In a previous study, Elastyrene® was dissolved after some minutes' contact with a monomer mixture of MMA (methyl methacrylate), EGDMA (ethylene glycol dimethacrylate), and 1,4 BDMA (1,4-butanediol dimethacrylate), probably due to the presence of MMA. Scanning with an electron microscope of the inside surface of glove materials before and after contact with a monomer mixture on the outside showed destruction in most materials (Lönnroth et al., 2002). Destruction enhanced the permeation of monomers, but also leakage of viruses, thus causing an additional hazard in dentistry.

The longest BTT and thus the best protection, was recorded for the 4 nitrile rubber gloves Nitra Touch, Nitril, Lirtin and N-Dex Nitrile, Tactylon® (styrene-ethylene-butadiene), and for Metin, the thickest poly (vinyl chloride) glove. Dental personnel prefer working with natural rubber latex gloves (Lönnroth & Shahnavaz, 1998b), probably due to good grip and fitting. The growing problem among health care personnel with skin problems and allergies due to frequent wearing of natural rubber latex gloves (Heese, Peters, Stahl, Koch, & Hornstein, 1995; Tarlo, Sussman, & Holness, 1997; Taylor & Praditsuwan, 1996) is of great concern among dental personnel. One solution might be using a nitril rubber glove as an inner glove, to avoid skin contact with natural rubber latex, and on top using a natural rubber latex glove to get a good grip. If using dry gloves however, the protection is equal to that of the better of the two materials, as shown by Lönnroth et al. (2002). In order to improve the protection against permeation by monomers they found that with wet interface, the BTTs increased significantly.

Breakthrough time (BTT) is used as a measure of protection and to compare materials based on the BTTs. The BTT is deemed to occur when the analytic equipment detects a permeation rate of $1 \mu\text{g min}^{-1} \text{cm}^{-2}$. However, the BTT cannot be seen as a “safe limit” to sensitized persons because small quantities of some monomers could be detected, but a BTT not determined, due to low permeation rate.

Gloves are used to prevent cross-contamination and to avoid skin contact with the potentially hazardous substances. It is recommended to select a glove with longest possible BTT, often change gloves, and not reuse disposable single gloves because the material might be affected due to previous contact with monomers. It can be concluded that Nitra Touch provided protection against all monomers in this study for at least 120 min, which will be sufficient in dental practice. However, nitrile rubber materials for dental use need to be improved to meet the requirements regarding fit and “feeling.”

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