Permeability of protective gloves by HEMA and TEGDMA in the presence of solvents

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Munksgaard EC. Permeability of protective gloves by HEMA and TEGDMA in the presence of solvents. Acta Odontol Scand 2000;58:57–62. Oslo. ISSN 0001-6357.

The breakthrough times and permeation rates of two commonly used allergenic components in dentin bonding agents or resins, HEMA and TEGDMA, were measured for 5 types of latex gloves and 5 types of nitrile gloves. In addition, the breakthrough times and permeation rates for the gloves were measured for HEMA and TEGDMA when diluted with either ethanol or acetone-solvents often appearing in dentin bonding agents. The mean breakthrough times for the 5 latex gloves for HEMA and TEGDMA, concentrated, diluted in ethanol, or diluted in acetone, were 4.9, 4.8, and 2.8 min, respectively. For the 5 nitrile gloves the equivalent breakthrough times were 15.7, 9.9, and 2.8 min, respectively. There were great variations between the various gloves, and 1 nitrile glove showed a breakthrough time of 28–30 min when tested with concentrated HEMA and TEGDMA. Compared to latex gloves, nitrile gloves have a longer-lasting protection against skin contamination with methacrylates in the absence of solvents. The longer protection was reduced or not present for methacrylates diluted in organic solvents, especially acetone. In addition, the nitrile gloves showed fairly high permeation rates in the presence of this solvent. The results indicate that latex and nitrile gloves only give a limited protection against allergenic methacrylates in dentin bonding agents when they contain acetone. □ *Diffusion; methacrylate resins; protective gloves*

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An increasing number of occupational dermatoses are caused by components in polymeric materials (1), and the dental profession suffers from an increase in the occurrence of skin diseases (2), among which a substantial number is caused by methacrylate-containing materials (3). Delayed hypersensibility (contact dermatitis) among dental personnel and patients can be induced by several methacrylates found in a number of dental materials. Methacrylates, known to induce allergy, are methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxypropyl-methacrylate (HPMA), 1,4-butanediol dimethacrylate (BUDMA), 1,6-hexanediol dimethacrylate, ethylene glycol dimethacrylate (EGDMA), triethylene glycol dimethacrylate (TEGDMA), 2,2-bis-[4-(2-hydroxy-3-methacryloyl-oxypropoxy) phenyl] propane (BISGMA), 1,6-bis-(methacryloyloxy-2-ethoxycarbonyl-amino)-2,4,4-trimethylhexane (UEDMA) and other urethane methacrylates (4–11). A questionnaire survey of Scandinavian prosthodontists revealed a high frequency of severe hand dermatoses and one of the predominant causes was contact with methacrylates (4). A questionnaire survey among Danish dentists proposed that around 2% of dentists suffer from dermatoses caused by methacrylate-containing materials (3).

Mono- and dimethacrylates are components of composite resins, bonding systems, resins and fissure sealants, as well as of materials used for orthodontic appliances, crowns and bridges, denture base, relining and repair, and as provisionals. Contact allergies among dentists induced by handling resinous dental materials are often characterized by their location on the first, second, and third fingers of the left hand. Contamination of these fingers happens during handling of the resin containers and during holding of the contouring strips while performing filling with resin composite (4, 9).

Studies performed on gloves used by surgeons have shown that MMA in bone cement readily penetrates the gloves and in some instances dissolves or damages the gloves (12, 13). One study (14) showed that MMA penetrates the gloves within 1 to 2.5 min. In a previous study (15), the breakthrough time for a number of latex and vinyl gloves was determined for concentrated methacrylate monomers. The study showed that for vinyl gloves the breakthrough time was between 1 and 3 min for HEMA and TEGDMA, and for latex gloves between 5 and 8 min. Reports (16–18) have shown that certain dental materials damage the protective gloves, leading to increased permeability of substances, including herpes virus. These latter studies indicate that methacrylates may show decreased breakthrough times when certain low molecular weight substances are present. Such substances are found in dentin bonding agents, which are often mixtures of methacrylates and ethanol or acetone.

The aim of this study was to measure the breakthrough time and permeation rate for the penetration of HEMA and TEGDMA, either concentrated or diluted with

Table 1. Specifications of the gloves used in the study

	Name of glove	Type	Manufacturer / distributor
A	Conform	Latex, powder	Ansell Edmont Indust., Aalst, Belgium
B	Safeskin LPE	Latex, powder	Safeskin Co., San Diego, CA, USA
C	Latexam	Latex, powder	Axel Madsen, Vedbæk, Denmark
D	Safeskin PFE	Latex	Safeskin Co., San Diego, CA, USA
E	Cenger Super gl.	Latex	Cenger Scandinavia, Stouby, Denmark
F	Safeskin Nitrile	Nitrile	Safeskin Co., San Diego, CA, USA
G	Profile 3000	Nitrile	Evergreen Europe ApS, Stouby, Denmark
H	N-dex	Nitrile	Best, Aartselaar, Belgium
I	Ansell TNT, powder	Nitrile, powder	Ansell Edmont Indust., Aalst, Belgium
J	Ansell TNT	Nitrile	Ansell Edmont Indust., Aalst, Belgium

ethanol or acetone, through gloves used by dental personnel. This is in order to establish safety limits for the time in which gloves can be worn after contamination with these methacrylates.

Materials and methods

HEMA, TEGDMA, ethanol, and acetone were obtained from Sigma-Aldrich Denmark A/S. Vejlegaardsvej 65B, DK-2665 Vallensbæk Strand, Denmark. Gloves were obtained from local dealers, and the names and types used in this study are listed in Table 1.

A diffusion chamber previously described (15) was used for the experiment. This was made of a beaker (diameter 3.5 cm, height 6.9 cm) equipped with a lid, in the centre of which a cylindrical tube made of polypropylene (diameter 1.66 cm, height 5.9 cm) was placed axially and in the centre of the beaker. The cylinder contained a magnetic stirrer on a perforated net, placed 4 mm from the bottom end; a magnetic stirrer was placed in the beaker as well. The beaker was filled with 20.00 ml deionized water. The thickness of the 3rd finger of a glove was measured using a gauge and placed around the bottom end of the cylinder and secured with a rubber ring. After placement, the thickness of the glove membrane on the cylinder was measured. The cylinder was then filled with 2.5 ml of a monomer mixture of HEMA and TEGDMA, 50 w/w% of each or with this mixture diluted to 50% with either ethanol or acetone. The glove membrane, having an area determined by the area of the end of the cylinder (2.16 cm^2), was located 1 cm above the bottom of the beaker. The pressure of water and that of the monomer mixture or solution on the glove membrane were practically equal; 100 µl aliquots of the aqueous liquid in the beaker were taken at certain periods using one of the following time intervals in minutes: 3–6–9–12–15–18, 6–9–12–15–18–21, 9–12–15–18–21–24, 15–20–25–30–35–40, or 25–30–35–40–45–50. The interval used for each experiment was chosen as the one in which the lowest number was higher than, but closest to, a breakthrough time (see below), which was roughly estimated in a preliminary experiment. The timing was started when the cylinder equipped with the glove membrane was filled with monomer mixture; the magnetic stirring was initiated at the same time. The methacrylate mixture and the water were preheated to 37°C, at which temperature the experiment was performed. Five separate experiments were performed for each glove and for the 3 mixtures of monomers.

The aliquots were analysed by HPLC. The concentration of a monomer in an aliquot was determined by comparing the peak height with that of known amounts of the monomer. The HPLC analysis was performed on an instrument (LKB/Pharmacia, Uppsala, Sweden) equipped with a pump, UV-detector, autosampler, integrator, and a reverse phase Sephacil C-18, 5 µm, 100 × 4 mm (Pharmacia) column. Fifty percent ethanol in water was used as solvent, the flow rate was 0.25 ml/min, and detection was performed at 210 nm. All measurements were performed in duplicate and as peak heights.

A plot of the height of the peak of a monomer (HEMA or TEGDMA) versus time of diffusion revealed a straight line, as the one seen in Fig. 1. The intersection of the line on the abscissa is the breakthrough time, representing the

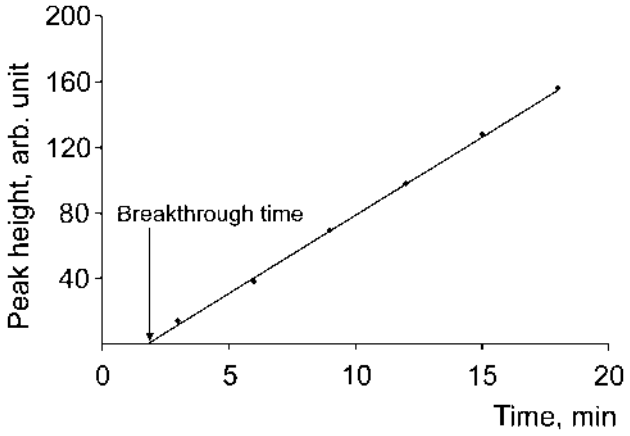

Fig. 1. Peak height in the aliquots taken from the water in the diffusion chamber versus time when a latex glove is used as membrane in the chamber. The intersection of the abscissa is the breakthrough time and the slope of the line is proportional to the permeation rate.

Table 2. Mean thickness in μm of each of gloves A–J at fingertip and mean thickness of the corresponding diffusion membrane in % of the thickness of the glove

	Thickness of glove		Thickness of the membrane in per cent of glove	
Glove	μm	SD	%	SD
A	101	0.4	73	18
B	241	1	84	13
C	179	1	83	8
D	241	1	86	5
E	228	1	88	7
F	163	1	84	6
G	175	1	89	5
H	201	0.4	89	7
I	176	1	81	7
J	171	1	89	9

time it takes for a monomer to diffuse through the membrane; the slope is a measure of the permeation rate. Based on a linear regression analysis, the mean breakthrough time and SD, as well as the mean permeation rate and SD, were calculated for each glove and for HEMA and TEGDMA, respectively. The mean breakthrough time was expressed in minutes and the permeation rate in μg monomer × cm^{-2} min^{-2}. The significance of the differences between the results obtained with the various gloves and the 3 solutions was determined by analysis of variance and by Newmann-Keuls' Multiple Range Test (19).

Results

Table 2 gives the thickness of the gloves at the fingertip and the stretching of the glove tip after positioning on the cylinder. On average, the glove membranes were streched about 15 (4.7)%. With the exception of glove A, the mean thickness of the membranes was 169 (26) μm. Figs 2–5 illustrate the breakthrough time (SD) for HEMA or TEGDMA concentrated, diluted in ethanol or in acetone when tested with the 5 latex and the 5 nitrile gloves.

Figs 2 and 4 represent 10 groups of results for gloves A–J with concentrated HEMA, HEMA in ethanol, and HEMA in acetone. Analysis of variance performed within each of the 10 groups in Figs 2 and 4, each comprising 3 sets of results, revealed for all groups *F*-values higher than 13.5, corresponding to *P*-values less than 8×10^{-4}. Since 10 analysis were performed, the level of significance was chosen as $P = 5 \times 10^{-3}$, and at this level the 3 measurements within each of the 10 groups differed significantly. Newmann-Keuls' Multiple Range Test showed that for groups A, B, and H, respectively, the results obtained with concentrated HEMA did not differ from those obtained with HEMA in ethanol, indicated by horizontal bars in the Figs.

Figs 3 and 5 represent similar results but with TEGMA concentrated, diluted in ethanol, or diluted in acetone. By

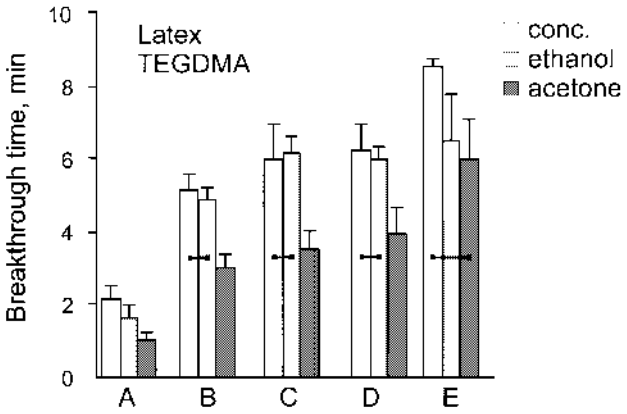

Fig. 3. The mean breakthrough time for latex gloves A–E with TEGDMA when tested concentrated, diluted in ethanol, and diluted in acetone. The horizontal bars indicate means that are not significantly different. The T-bars are the standard deviations.

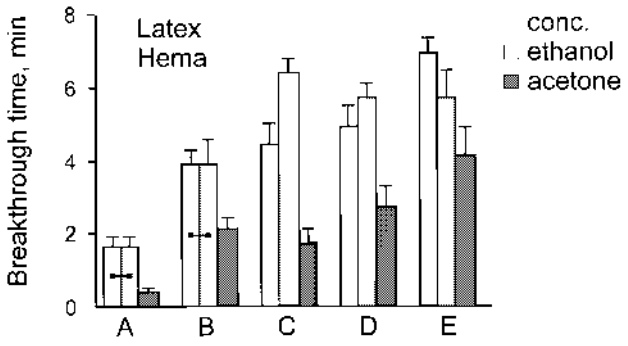

Fig. 2. The mean breakthrough time for latex gloves A–E with HEMA when tested concentrated, diluted in ethanol, and diluted in acetone. The horizontal bars indicate means that are not significantly different. The T-bars are the standard deviations.

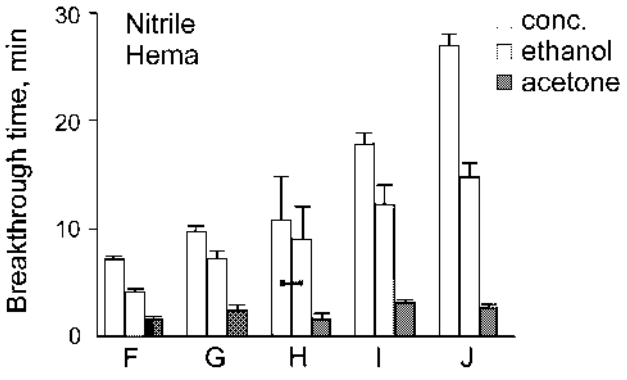

Fig. 4. The mean breakthrough time for the nitrile gloves F-J with HEMA when tested concentrated, diluted in ethanol, and diluted in acetone. The horizontal bar indicates means that are not significantly different. The T-bars are the standard deviations.

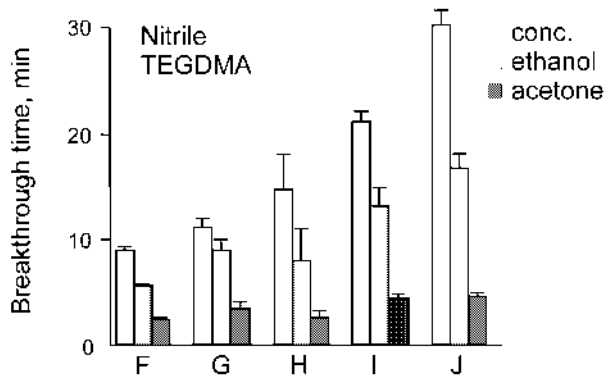

Fig. 5. The mean breakthrough time for nitrile gloves F–J with TEGDMA when tested concentrated, diluted in ethanol, and diluted in acetone. The T-bars are the standard deviations.

analysis of variance performed as above, it was shown that the *P*-values were lower than 5×10^{-3}, except for glove E. The results from the multiple range tests, performed on each of the remaining 9 groups, showed that for groups B, C, and D, respectively, the results obtained with concentrated TEGDMA did not differ from those obtained with TEGDMA in ethanol, indicated by horizontal bars in the Figs.

The variation between the individual gloves (latex and nitrile), when tested with concentrated HEMA or TEGDMA, HEMA or TEGDMA in ethanol, or HEMA or TEGDMA in acetone, was estimated by analysis of variance and the multiple range test. The results are given in Table 3. Table 4 gives the permeation rates for the 5 latex and the 5 nitrile gloves when tested by the three solutions.

Discussion

Dentists use protective gloves predominantly to reduce spreading of bacteria and vira, but also to avoid contamination of the fingers with chemicals, including allergenic substances. Since the dental profession suffers from an increase in the prevalence of skin diseases caused by dental materials, including methacrylate-containing products (1–13), it is of interest to know the period for which a glove protects against methacrylates.

In the last decade, nitrile gloves have been introduced as a substitute for latex gloves. Nitrile compared to latex gloves has the advantage of not inducing the common glove type 1 allergy, since they do not contain proteins as in latex. In addition, nitrile gloves compared to latex gloves are claimed to show much longer breakthrough times for a number of chemicals (20), including methyl methacrylate. Reports (16–18) showing that certain dental materials damage the protective gloves leading to an increased permeability are the reason for measuring the breakthrough time for HEMA and TEGDMA in the presence of ethanol or acetone. Especially HEMA is present in many dentin bonding agents, along with ethanol or acetone; TEGDMA is predominantly found in resins and resin composites (21).

The method used in this investigation differs from other methods used in this area (22) by using the fingertip, which were stretched to about 15% (Table 2). This was chosen in order to mimic the situation where a dentist contaminates the finger tip of the glove with a methacrylate-containing product, and where the glove on the fingers is stretched in order to maintain proper tactility. It is known (16–18) that chemicals will change the gloves, leading to increased permeability the longer the chemicals are in contact (15). This was the reason for choosing individual intervals, depending on type of glove, within which aliquots for analysis were taken from the water into which the substances diffused. The interval for a specific glove was chosen as being close to the breakthrough time estimated roughly in a preceding experiment. If longer intervals had been used, the curve by which the permeation rate was measured (Fig. 1) would probably not have been linear. In addition, with longer intervals one may reach the solubility of TEGDMA in water (3 mg/ml). In the present experiments, the highest measured TEGDMA concentration was 0.4 mg/ml.

It is generally acceptable to measure breakthrough times

Table 3. Result from statistical analysis of the mean breakthrough times for the 10 gloves (A–J) when tested with either HEMA or TEGDMA and when these are either concentrated or diluted in solvents. The mean breakthrough times for gloves within each column and which are designated with the same symbol (*, †, ‡, or §) are not significant different

HEMA, conc.	HEMA, ethanol	HEMA, acetone	TEGDMA, conc.	TEGDMA, ethanol	TEGDMA, acetone
A	A	A	A	A	A
B*	B*	B†‡	B*	B*	B*†
C*	C†	C*†	C*	C*†	C†‡
D*	D†	D‡§	D*	D*	D‡§
E†	E†	E	E†	E*†	E
F†	F*	F*†	F†‡	F*	F*
G‡	G†	G‡	G‡	G‡	G†‡
H‡	H	H*	H	H†‡	H*
I	I	I§	I	I	I§
J	J	J‡§	J	J	J§

Table 4. Permeation rates (SD) in μg cm^{-2} min^{-1} through gloves A–J for HEMA and TEGDMA when concentrated or diluted in ethanol or acetone

	HEMA, concentrated		HEMA, in ethanol		HEMA, in acetone		TEGDMA, concentrated		TEGDMA, in ethanol		TEGDMA, in acetone	
Glove	Rate	SD	Rate	SD	Rate	SD	Rate	SD	Rate	SD	Rate	SD
A	30.6	7.7	15.7	3.2	64.4	18.8	26.0	6.4	20.8	4.4	34.4	7.1
B	20.1	3.2	11.2	2.2	38.0	2.9	17.7	3.3	13.0	1.2	23.5	1.6
C	21.9	8.5	19.8	8.9	40.8	8.8	15.0	6.5	14.1	5.1	16.5	3.8
D	15.4	2.2	8.2	1.9	29.7	3.7	12.9	1.8	9.3	2.1	15.9	1.3
E	15.7	4.3	8.6	3.7	28.0	4.9	10.6	3.4	8.8	4.0	14.7	2.4
F	91.2	27.2	70.9	5.1	709.1	51.5	27.3	9.3	27.4	3.7	139.5	10.1
G	71.4	44.0	68.3	14.5	768.8	97.0	22.2	12.7	26.2	5.2	171.4	25.5
H	223.0	20.2	134.7	16.9	733.2	30.9	93.7	13.7	60.8	4.8	193.3	29.2
I	87.0	28.7	117.4	6.4	686.6	197.6	31.1	11.0	51.6	1.8	157.5	34.6
J	55.6	12.0	145.1	10.2	680.6	11.1	16.0	3.7	64.0	2.6	189.0	14.8

by methods such as that described in Fig. 1 inasmuch as the "real" breakthrough time is a little shorter. This is because it takes some time to reach a steady state condition characterized by linearity as the one shown by the figure. The exact breakthrough times can be estimated by measuring diffusion at much shorter time intervals, but for practical purposes the way used in this study is judged appropriate.

The results show that nitrile gloves generally have longer breakthrough times than latex gloves (Figs 2–5 and Table 3). On comparing the results shown in Figs 2–5, only small differences can be seen between the results obtained with HEMA compared to those obtained with TEGDMA. Of the 5 latex gloves, glove E showed the highest breakthrough time with concentrated HEMA or TEGDMA (7–8 min), and of the 5 nitrile loves, glove J has the highest breakthrough time (28–30 min). Gloves B and D differ only in that the latter contains powder. This is also the case for gloves I and J. In both cases, the gloves without powder showed the longest breakthrough time. This difference in breakthrough time can be explained by the treatment of the powder-free gloves by the manufacturer. In order to obtain a smooth non-sticky internal surface, the gloves are treated with chlorine, for example. Such treatment might decrease the permeability of the glove.

The results from the latex gloves presented in Figs 2 and 3 show that the breakthrough times for HEMA and TEGDMA in 6 out of 10 cases were not significantly different from the breakthrough times for the substances diluted with ethanol. In 9 out of the 10 cases a significant difference was observed on comparing the results obtained with the concentrated material with those obtained with the material diluted in acetone. It can be calculated from the results that the mean breakthrough times through the 5 latex gloves for HEMA and TEGDMA, concentrated, diluted in ethanol or diluted in acetone were 4.9, 4.8, and 2.8 min, respectively.

The results from the nitrile gloves presented in Figs 4 and 5 show that only for glove H did no significant difference appear between the breakthrough time estimated with concentrated HEMA and with HEMA in ethanol. As above, it can be calculated that the mean breakthrough times through the 5 nitrile gloves for HEMA and TEGDMA, concentrated, diluted in ethanol, or diluted in acetone were 15.7, 9.9, and 2.8 min, respectively.

As mentioned above, the breakthrough times are

Table 5. Permeation coefficients in cm/min calculated on the basis of the rates given in Table 4

	HEMA			TEGDMA		
Glove	Conc.	Ethanol	Acetone	Conc.	Ethanol	Acetone
A	*$6.1\ 10^{-5}$	*$6.3\ 10^{-5}$	$2.6\ 10^{-4}$	$5.2\ 10^{-5}$	$8.3\ 10^{-5}$	$1.4\ 10^{-4}$
B	†$4.0\ 10^{-5}$	†$4.5\ 10^{-5}$	$1.5\ 10^{-4}$	$3.5\ 10^{-5}$	$5.2\ 10^{-5}$	$9.4\ 10^{-5}$
C	$4.4\ 10^{-5}$	$7.9\ 10^{-5}$	$1.6\ 10^{-4}$	$3.0\ 10^{-5}$	$5.6\ 10^{-5}$	$6.6\ 10^{-5}$
D	‡$3.1\ 10^{-5}$	‡$3.3\ 10^{-5}$	$1.2\ 10^{-4}$	$2.6\ 10^{-5}$	$3.7\ 10^{-5}$	$6.4\ 10^{-5}$
E	§$3.1\ 10^{-5}$	§$3.4\ 10^{-5}$	$1.1\ 10^{-4}$	$2.1\ 10^{-5}$	$3.5\ 10^{-5}$	$5.9\ 10^{-5}$
F	$1.8\ 10^{-4}$	$2.8\ 10^{-4}$	$2.8\ 10^{-3}$	$5.5\ 10^{-5}$	$1.1\ 10^{-4}$	$5.6\ 10^{-4}$
G	$1.4\ 10^{-4}$	$2.7\ 10^{-4}$	$3.1\ 10^{-3}$	$4.4\ 10^{-5}$	$1.0\ 10^{-4}$	$6.9\ 10^{-4}$
H	$4.5\ 10^{-4}$	$5.4\ 10^{-4}$	$2.9\ 10^{-3}$	$1.9\ 10^{-4}$	$2.4\ 10^{-4}$	$7.7\ 10^{-4}$
I	$1.7\ 10^{-4}$	$4.7\ 10^{-4}$	$2.7\ 10^{-3}$	$6.2\ 10^{-5}$	$2.1\ 10^{-4}$	$6.3\ 10^{-4}$
J	$1.1\ 10^{-4}$	$5.8\ 10^{-4}$	$2.7\ 10^{-3}$	$3.2\ 10^{-5}$	$2.6\ 10^{-4}$	$7.6\ 10^{-4}$

Coefficients for the same type of glove and monomer not differing more than 10% are designated with a symbol (*, †, ‡, or §).

generally higher for the nitrile gloves than for latex gloves, but this seems not to be the case when tested in the presence of acetone. The average breakthrough times for the latex and nitrile gloves were in both cases 2.8 min. A remarkable difference exists between the permeation rates for the latex and the nitrile gloves. The nitrile gloves generally show much higher permeation rates (Table 4) than latex gloves. This implies that after the breakthrough time has elapsed, greater contamination of the fingers might appear with nitrile gloves than with latex gloves. In addition, the permeation rate of HEMA was generally faster than that of TEGDMA.

It can be concluded that the breakthrough times for HEMA and TEGDMA are generally higher for the nitrile gloves than for the latex gloves, but not when the substances are diluted with acetone, in which case relatively short breakthrough times were measured. This could imply that the gloves give only limited protection against methacrylates in dentin bonding agents containing acetone. Nevertheless, there is great variation among the various brands of gloves. The nitrile gloves generally showed much higher permeation rates than the latex gloves.

Acknowledgement.—Technical assistant Liselotte Larsen is complimented for care and competence during the performance of the experiments.

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Received for publication 4 November 1999
Accepted 25 January 2000