

Swelling of Polymeric Glove Materials during Permeation by Solvent Mixtures

L. B. Georgoulis,¹ M. S. Morgan,¹ N. Andrianopoulos,² J. C. Seferis³

¹Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, Washington 98195

²National Technical University of Athens, Greece

³Department of Chemical Engineering, University of Washington, Seattle, Washington 98195

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ABSTRACT: Extrapolation from permeation data for pure solvents does not predict accurately their behavior in mixtures. In this study we examined whether the permeation of natural rubber, nitrile, and PVA glove materials by solvent mixtures is proportional to material swelling. Gloves were exposed to solvent mixtures and their permeation was monitored: breakthrough times, permeation rates, and degree of swelling were determined. Toluene exhibits higher permeation than MEK through natural rubber. Adding MEK to toluene decreased the permeation of toluene and increased that of MEK, proportionally to mixture composition and the degree of swelling. The opposite was observed for nitrile: toluene, now the "low permeation" solvent (LPS), retarded MEK permeation and vice versa. The effect was proportional

to mixture composition but not consistently proportional to the degree of swelling. Samples were also exposed to the LPS for different time periods prior to a permeation run using the "high permeation" solvent (HPS). The decrease in breakthrough time of the HPS was proportional to the degree of swelling caused by the LPS. Material swelling appears to control MEK and toluene permeation through natural rubber. For nitrile, additional factors are apparently at work. No permeation was detected through PVA and material swelling was negligible. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 775–783, 2005

Key words: diffusion; gloves; nanotechnology; rubber; swelling

INTRODUCTION

The dermal route of exposure is significant in many industrial operations. Dermal contact with hazardous materials can lead to a variety of adverse health effects, ranging from simple skin irritation to allergic reactions, burns, and chronic diseases such as cancer. In the United States from 1990 to 2000, an average of 60,000 incidents of occupational skin diseases have been reported each year, which is almost 20% of all occupational illnesses.¹ This incidence rate is the second highest, preceded only by repeated trauma disorders. The majority of all the skin diseases occurring in work places are hand related. Berardinelli² reported that 70 to 80% of occupational contact dermatitis involves the hands.

Although there is considerable scientific literature on the permeation of chemical protective clothing (CPC) and/or gloves by solvents, very little research has dealt with the behavior of solvent mixtures. A thorough literature search resulted in only eight studies that have examined the effects of multicomponent

mixtures.^{3–10} All of them have shown that extrapolation from the pure solvent permeabilities does not predict accurately the behavior of the mixture.

Despite the limited available research, the majority of industrial processes involve exposure to liquid solvent mixtures rather than pure solvents. Examples of such processes include the handling of paints and thinners, fuels, hazardous waste, solvent cleaning mixtures, etc. MEK and toluene were chosen for this study because the 50–50% mixture is used by commercial airplane manufacturers to clean and degrease airplane parts prior to painting.

Permeation can be described as a three-step process during which molecules of a chemical move through a protective material.^{2,7,11} The chemical is absorbed at the outside surface of the material, diffuses through the material matrix, and finally desorbs from the inside surface of the protective material. Permeation should not be confused with penetration, which refers to the bulk flow of a chemical through holes, pores, seams, and imperfections in the protective material on a non-molecular level.

The two permeation measurements most often reported in the literature are breakthrough time and permeation rate. Breakthrough time is the elapsed time between initial contact of the chemical with the outer surface of the glove and its detection at the inner

Correspondence to: J. C. Seferis.

TABLE I
Tested Gloves

Glove material	Catalog name	Catalog no.	Mean measured thickness (mm)
Natural rubber	Orange heavyweight	208	0.83
Nitrile rubber	Sol-Vex®	37-155	0.49
PVA (polyvinyl alcohol)	PVA™ coated	15-552	0.92

surface. Permeation rate is defined as the mass of solvent passing through a given surface area of the glove material per unit time.

Permeation rates and breakthrough times of polymeric glove materials by a given challenge solution depend on a number of factors: temperature,¹²⁻¹⁵ material thickness,^{12,16-19} mechanical stress,^{15,20} glove manufacturer,^{15,21,22} the part of the glove from which the sample is taken,²³ and possibly humidity and moisture.²⁴

Wiemann⁶ proposed a model to explain the increased permeation of solvent mixtures with regard to the pure compounds. It was based on the observation that pure compounds with a high permeation rate through a glove material cause the material to swell during permeation. In a binary mixture composed of a high and a low permeation rate component, at steady state, the low permeation rate solvent may diffuse more rapidly due to swelling caused by the high permeation rate solvent.

This study consisted of two parts. The purpose of the first part was to characterize the interaction between MEK and toluene as they permeate through three different glove materials and to quantify the effects of glove material swelling on the solvents' permeation rates. The hypothesis tested was that high degrees of swelling should be correlated with high permeation rates. The aim of the second part was to study the effect of prior swelling of the glove materials by one of the solvents on the breakthrough time of the other. The hypothesis was that the longer the glove sample has been exposed to the first solvent (and therefore the more the glove material has swollen) the shorter the breakthrough time of the second solvent.

METHODS

Materials and instrumentation

Three different glove materials were tested, all obtained from Ansell Edmont Industrial (Table I). The permeation experiments were based on the American Society for Testing and Materials (ASTM) standard method,²⁵ using a modified permeation cell (Fig. 1).

The experimental setup consisted of the following instruments, connected in an open loop configuration (Fig 2): the source of the carrier gas (compressed nitrogen), a flow valve, a rotameter, the permeation cell, a liquid trap, two MIRANs, an A/D converter, and a computer. The first MIRAN was set up to measure MEK and the second to measure toluene. Teflon tubing with stainless steel, brass, and teflon fittings were used throughout the system.

The flow of the carrier gas was set to 5.76 L/min. For the chosen flow, the transport times from the permeation cell to the first and then the second MIRAN were determined to be 5 and 30 s, respectively. These transport times were not more than 1/4 of the shortest observed breakthrough times (1.1 min for MEK and 2.1 min for toluene).

For each solvent an optimum analytical wavelength was chosen based on the transmittance spectrum: 8.55 μm for MEK and 13.9 μm for toluene. Special consideration was given to choosing a wavelength at which spectral overlap between the two solvents is minimal.

To maximize sensitivity in detecting the initial breakthrough of the solvents, a long path length was chosen, namely 20.25 m. However, at this path length the instrument response would easily exceed the linear absorbance range with increasing solvent concentrations during the permeation runs. To overcome this problem, during each run and just before the instruments reached full scale (absorbance of 1.0), the path length was changed to 0.75 m. In accordance each instrument was calibrated at both path lengths.

To quantitate the spectral overlap of the two solvents, each MIRAN was also calibrated, at both path lengths and over the entire range of concentrations, using the second solvent. In other words, the first MIRAN set at the MEK optimum wavelength and gain was calibrated with toluene and vice versa. Based on these calibration equations, spectral overlap during

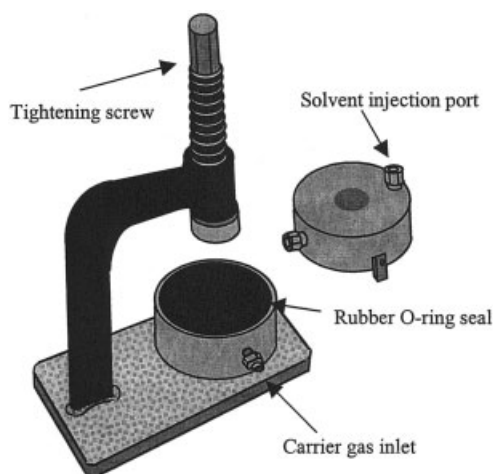


Figure 1 Permeation cell.

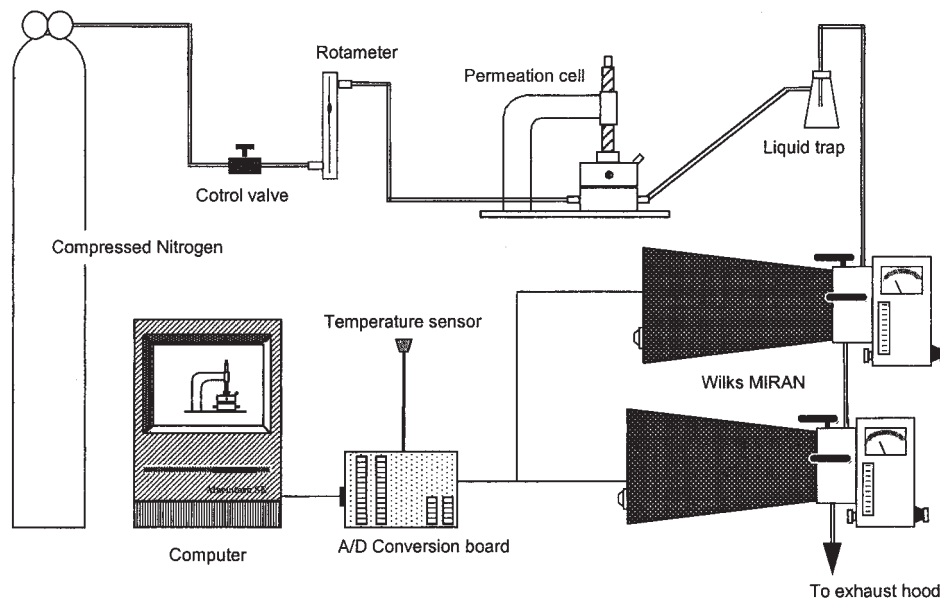


Figure 2 Experimental setup.

the actual experiments was determined to be in the order of 1–6%.

Procedures: solvent mixtures runs

For the first set of experiments, five solvent mixtures were tested: 100% MEK, 100% toluene, 50–50%, 25–75%, and 75–25% (by volume). Five natural rubber, five nitrile, and three PVA glove samples were tested with each mixture. A circular sample from the glove palm, approximately 45.4 cm², was cut and inspected visually for defects and imperfections. The thickness of the specimen was measured at nine random locations using a thickness gauge capable of measuring to 0.001 inches. The average, converted to millimeters was reported. Finally, three pairs of marks, AB = 1 cm, CD = 2 cm, and EF = 3 cm were placed on the inner surface of the sample using a ballpoint pen.

The glove sample was placed in the permeation cell with the outer surface facing up and the cell was clamped to a reproducible torque using an adjustable torque screwdriver. Once in the permeation cell, only an area of 19.44 cm² of the glove sample was actually exposed. The N₂ flow was set to 5.76 L/min. Ten milliliters of the challenge solution was injected through the injection port and the port was immediately capped to minimize evaporation of the solvents during the run.

At the same time the computer data acquisition program was activated to record the reading of the two MIRANs every 5 s. Each run lasted a maximum of 4 h. It was discontinued earlier if the permeation of both solvents had reached either a steady state or a maximum.

At the end of each run, the amount of solvents remaining in the upper part of the permeation cell was discarded and the glove sample was removed and patted dry. The thickness of the sample was measured again at nine random locations and the new distances of the paired marks were recorded. The degree of swelling was then determined as percent increase in thickness [eq. (1)] and mean percent increase in the lateral dimension [eq. (2)].

$$\left(\frac{\text{Thickness}_{\text{after}} - \text{Thickness}_{\text{before}}}{\text{Thickness}_{\text{before}}} \right) \times 100 \quad (1)$$

$$\frac{\left(\frac{AB_{\text{after}} - AB_{\text{before}}}{AB_{\text{before}}} \right) + \left(\frac{CD_{\text{after}} - CD_{\text{before}}}{CD_{\text{before}}} \right) + \left(\frac{EF_{\text{after}} - EF_{\text{before}}}{EF_{\text{before}}} \right)}{3} \times 100 \quad (2)$$

The breakthrough time and the steady state or maximum permeation rate for each solvent were calculated from the graph data. Breakthrough time was arbitrarily defined as the elapsed time from the beginning of the run to when each MIRAN first recorded a concentration of 5 ppm of solvent in the carrier gas, adjusted for transport time. The chosen concentration of 5 ppm was well above the detection limit of the instruments, which was determined to be approximately 1 ppm for both solvents.

Because the three glove materials used had different thickness, the breakthrough time (min) was divided

by the square of the thickness before swelling (mm) to yield a "thickness adjusted" breakthrough time. This term was preferred over "normalized" breakthrough time used by other authors^{7,12,19} because the latter has a different definition in the standard method.²⁵ The steady state or maximum permeation rate (J) was calculated using the guidelines of the American Society for Testing and Materials²⁵ [eq. (3)]:

$$J = \frac{C \times Q}{A} \quad (3)$$

where C is the concentration of the chemical in the carrier stream, $\mu\text{g/L}$; Q is the flow rate of the carrier steam, 5.76 L/min; and A is the area of the glove material exposed to the solvent, 19.44 cm^2 .

During each permeation run the temperature was also monitored. For the entire duration of the experiments (6 months) it ranged from 21.9 to 23.8°C, with an average of 22.7°C. Although temperature is known to effect the permeation through glove materials, the influence of the small differences observed should be minimal.¹³

Procedures: preswelling runs

In the second part of the experiments only natural rubber and nitrile rubber gloves were used. The glove sample was again measured for thickness and lateral dimension, placed in the permeation cell, as previously described, and the lower part of the cell was flushed with a constant airflow of approximately 5 L/min. An amount of one of the solvents, called the "swelling solvent," was injected in the upper part of the permeation cell and allowed to remain there for three predetermined time periods producing "no,"

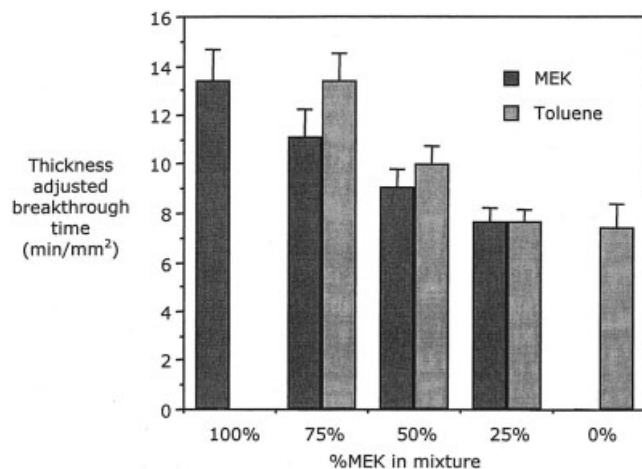


Figure 3 Effect of mixture composition on "thickness adjusted" breakthrough times through natural rubber. Each bar is the average of five measurements. Error bars represent the SD.

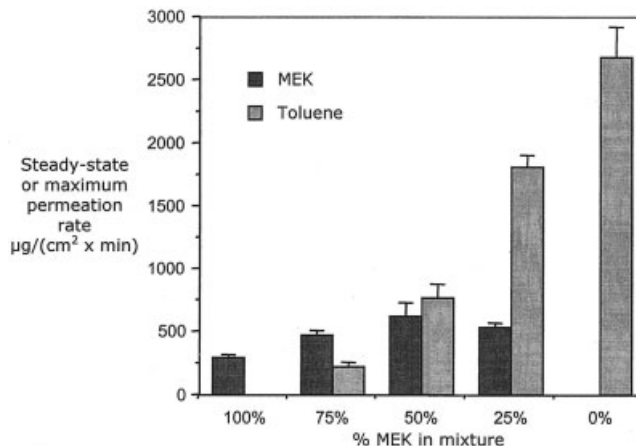


Figure 4 Effect of mixture composition on permeation rates through natural rubber. Each bar is the average of five measurements. Error bars represent the SD.

"moderate" (approximately 4%), and "complete" (10–20%) swelling. For each "swelling period" five natural rubber and five nitrile gloves were tested.

The "swelling solvent" was removed and the degree of swelling of the glove material was measured according to the procedures mentioned above. The sample was immediately replaced in the permeation cell, 10 ml of the second solvent was injected and a permeation run was initiated, as described earlier. For the samples exposed to the "swelling solvent" for a "complete swelling" period and while the instrument was set at 20.25 m, the interference due to spectral overlap was significant and therefore was subtracted from the reported concentrations. Care was taken to keep the time from the removal of the first solvent to the injection of the second solvent and the initiation of the permeation run as brief as possible and always below 5 min.

MEK was chosen as the "swelling solvent" applied on natural rubber, whereas toluene was used with nitrile. To determine the appropriate exposure times leading to "moderate" and "complete" swelling for each glove/solvent combination, a series of preliminary experiments was performed, to document the swelling profiles through time. Based on these results, for the MEK/natural rubber system 5 min was chosen for "moderate" (approximately 4%) and 50 min for "complete" (10–20%) swelling. For toluene and nitrile rubber 5 min and 80 min were chosen, respectively. For both systems no prior exposure (0 min) represented "no" swelling.

RESULTS

Natural rubber

Toluene exhibited lower "thickness adjusted" breakthrough times and higher permeation rates compared

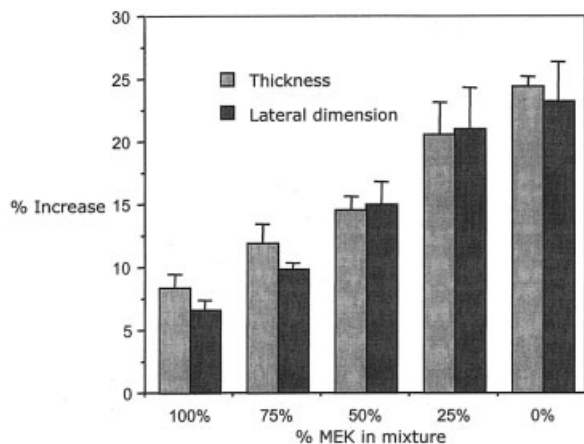


Figure 5 Effect of mixture composition on natural rubber swelling. Each bar is the average of five measurements. Error bars represent the SD.

to MEK. However, adding MEK to toluene decreased the permeation ability of toluene and increased that of MEK (Fig. 3 and 4). The effect appears to be related to the composition of the mixture. After log transformation of the data, an analysis of variance (ANOVA) for the “thickness adjusted” breakthrough times and maximum permeation rates of both solvents showed that, in all cases, the effect of mixture composition was significant. Since the groups were ordered, studying the possibility that there is a linear trend across them is a better approach than comparing each pair of groups using a post hoc test.²⁶ In all four cases there was a highly significant linear trend. However, in three out of four cases (MEK “thickness adjusted” breakthrough times was the only exception), the non-linear variation between the groups was also significant, indicating that the linear trend only explains some of the effect of mixture composition.

A similar pattern was found in the degree of swelling of the glove material. As the percent of toluene, the “high permeation” solvent in the mixture, increased, the degree of swelling of the material also increased in linear fashion (Fig. 5).

When the individual values of the increase in thickness were plotted against the cumulative permeation rate for each permeation run, i.e., the sum of the steady state or maximum permeation rate of both solvents, a very strong correlation was revealed (Fig. 6). The same effect was seen when the cumulative permeation rates were plotted against the percent increase in the lateral dimension. Breakthrough times were also strongly correlated to the degree of material swelling. The higher the increase in thickness due to exposure to MEK the lower the breakthrough time of toluene (Fig. 7). The same effect was observed when the thickness adjusted breakthrough times were plotted against the percent increase in the lateral dimension.

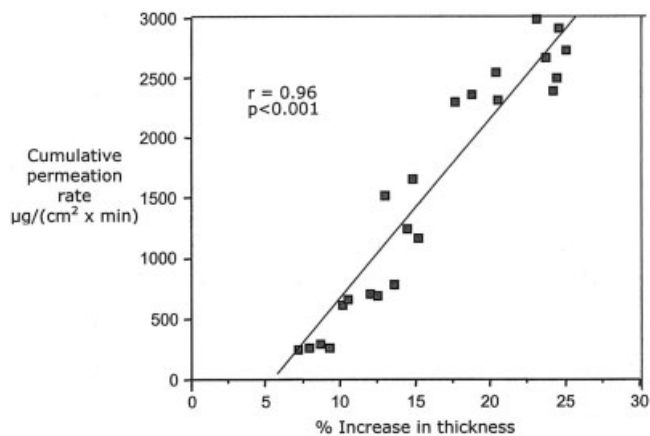


Figure 6 Effect of increase in thickness on the permeation rates through natural rubber. r is Pearson’s correlation coefficient.

Finally, the data from the two measures of glove material swelling, caused by exposure to the five mixtures, were plotted against each other and a linear regression line was fitted to them (Fig. 8). The line was forced to pass through the origin, because swelling of the glove material is by definition zero in both dimensions when the sample has not been exposed to any solvents. The fit of the line is once again very strong and the slope (0.96) is statistically equal to one, suggesting that natural rubber swelling is isotropic, i.e., occurs equally in both dimensions.

Nitrile rubber

Overall, the effect of mixture composition was very similar to what was described above for natural rubber. However, this time the behavior of the pure solvents was reversed. MEK, now the “higher perme-

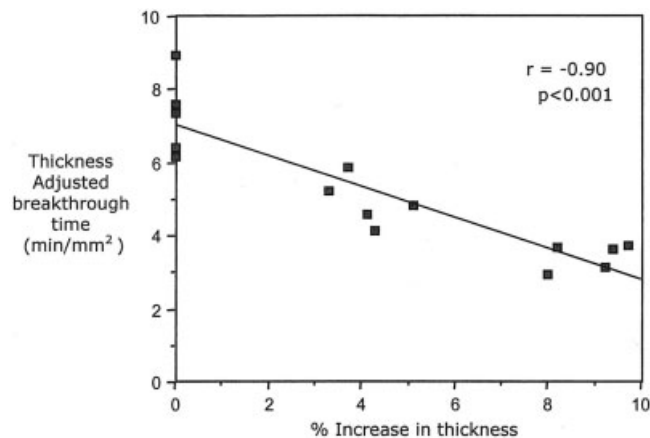


Figure 7 Effect of prior swelling by MEK on toluene breakthrough times through natural rubber as demonstrated by the increase in thickness. r is Pearson’s correlation coefficient.

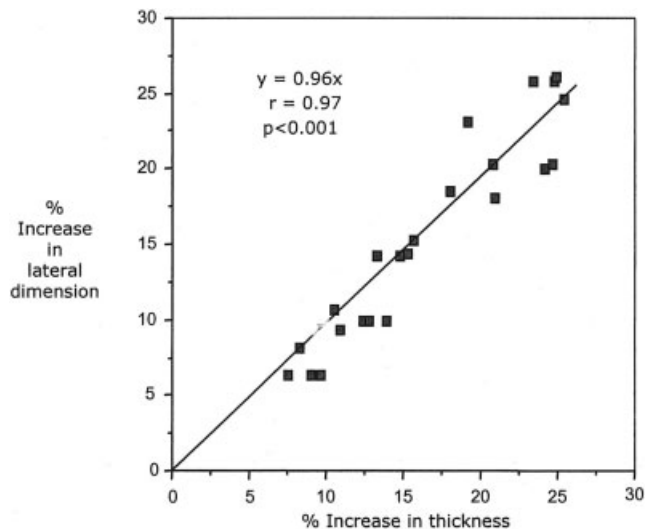


Figure 8 Swelling of natural rubber due to exposure to MEK and toluene mixtures.

ation" solvent, facilitated the permeation of toluene, whereas toluene, now the "lower permeation" solvent, retarded MEK (Fig. 9). The effect was again proportional to the composition of the mixture and highly statistically significant as revealed by the ANOVA of the log transformed thickness adjusted breakthrough times and maximum permeation rates of both solvents. As with natural rubber, in all four cases there is a statistically significant linear trend across the groups but the nonlinear variation was also significant.

Contrary to natural rubber, the degree of swelling for nitrile rubber is not consistently dependent on the composition of the solvent mixtures (Fig. 10). For the increase in thickness there is a linear trend but in the opposite direction: material swelling increased as the amount of the slow permeating solvent in the mixture

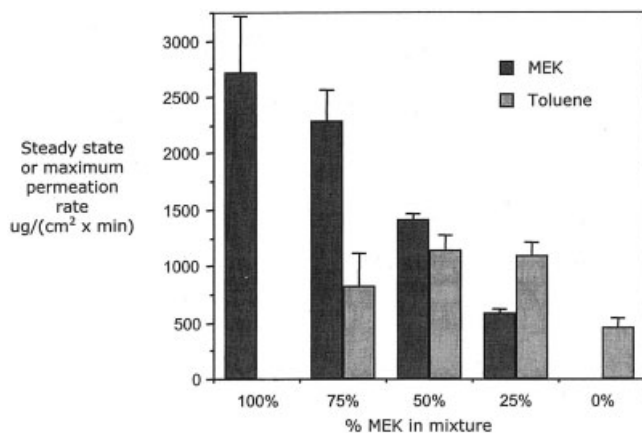


Figure 9 Effect of mixture composition on permeation rates through nitrile. Each bar is the average of five measurements. Error bars represent the SD.

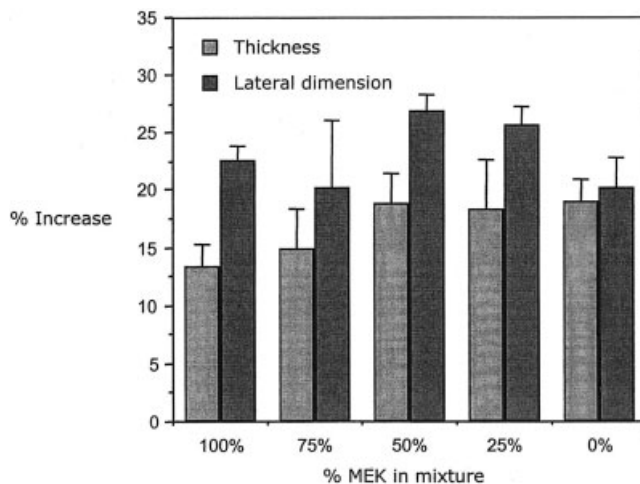


Figure 10 Effect of mixture composition on nitrile swelling. Each bar is the average of five measurements. Error bars represent the SD.

increased. For the increase in the lateral dimension on the other hand, a linear trend test showed the variation between the four mixture groups to be completely nonlinear.

In contrast to permeation rates, which did not show a consistent correlation to the degree of swelling, breakthrough times appear to be more consistent. Plotting the individual thickness adjusted breakthrough times of MEK versus the degree of swelling caused by toluene revealed the same effect that was observed for natural rubber. As the degree of swelling due to exposure to toluene increased, the breakthrough time of MEK decreased in a linear fashion.

Finally, the data from the two measures of glove material swelling caused by MEK and toluene mix-

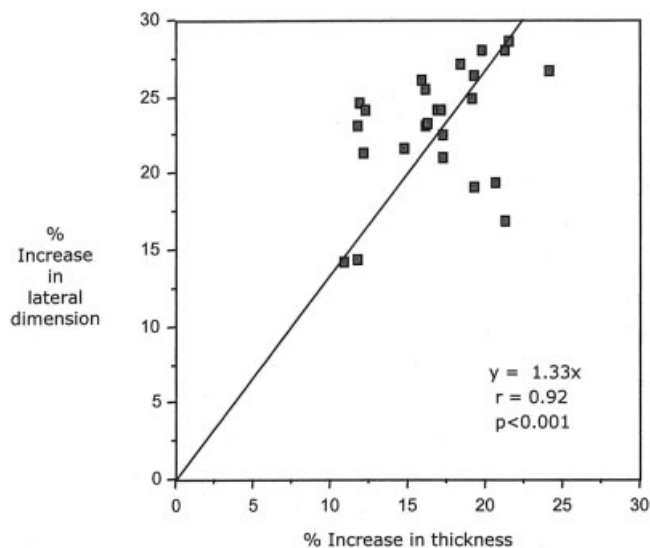


Figure 11 Swelling of nitrile due to exposure to MEK and toluene mixtures.

tures were plotted against each other (Fig. 11). A linear regression line, forced to pass through the origin, was fitted to the data. However, the slope of the line (1.33) was statistically different from one, suggesting that nitrile rubber swelling, contrary to natural rubber, is not equal in both dimensions (nonisotropic).

PVA

No permeation by any of the solvents was detected through PVA after exposure to all five solvent mixtures for 4 h. At the same time the swelling of the material was negligible. An increase in thickness of approximately 2.5% and a decrease of the same order in the lateral dimension was observed.

DISCUSSION

The results of these experiments support what has been shown in previous studies on the permeation of glove materials by binary solvent mixtures: extrapolation from the pure solvent's permeability does not predict accurately the behavior of the mixture. In the case of MEK and toluene mixtures through natural rubber and nitrile rubber the "higher permeation" solvent enhances the permeability of the "lower permeation" solvent. At the same time, the "lower permeation" solvent decreases the permeability of the "higher permeation" solvent. For both glove materials the effect is strongly dependent on the composition of the mixtures. The main difference between the two glove materials is which solvent is permeating more easily through which material. This may be related to the chemical structure of the solvents and the monomers of the glove materials: the nonpolar solvent (toluene) permeates more easily through natural rubber, which has a nonpolar monomer, whereas MEK, which is polar, permeates more easily through nitrile rubber whose monomer is also polar.

The results obtained for natural rubber provide some very strong evidence that material swelling must be the major factor controlling the permeation of these mixtures. As the percentage of toluene, the "higher permeation" solvent, in the mixture increases, the degree of swelling of the material also increases (Fig. 5). Additionally, high degrees of swelling are very strongly correlated with both short breakthrough times and high permeation rates (Figs. 6 and 7). Finally, material swelling occurs equally in all directions (Fig. 8).

For nitrile on the other hand, the relation is not so clear. As the percentage of the "higher permeation" solvent (MEK) in the mixture increases, the degree of swelling of the material follows either no pattern, as exemplified in the case of the increase in the lateral dimension, or shows a clear linear trend, but toward smaller values (Fig. 10). When nitrile rubber is ex-

TABLE II
Breakthrough Times (min) of MEK and Toluene Mixtures through Natural Rubber, Nitrile, and PVA

Natural rubber					
MEK	100%	75%	50%	25%	0%
	9.5	7.7	6.0	5.6	—
Toluene	0%	25%	50%	75%	100%
	—	9.4	6.6	5.6	5.0
Nitrile rubber					
MEK	100%	75%	50%	25%	0%
	6.4	6.7	8.8	12.0	—
Toluene	0%	25%	50%	75%	100%
	—	8.2	9.7	12.2	27.6
PVA	> 4 h for all mixtures				

posed to toluene alone, material swelling at steady state appears to be isotropic (Fig. 10). A paired *t* test showed the increase in thickness to be statistically the same as the increase in the lateral dimension ($P = 0.63$). However, when MEK is added to the mixture, swelling becomes nonisotropic, with the increase in the lateral dimension being more pronounced (Fig. 10 and 11). This suggests that MEK may cause some kind of structural modification of the glove material, causing it to swell more in the lateral dimension.

Glove selection

Although the "thickness adjusted" breakthrough time is useful for comparing the properties of different glove materials, it does not show directly the protection provided by the selected glove. Table II presents the actual breakthrough times of MEK and toluene through the three gloves used in this study. Based on this table the PVA gloves are clearly the best choice for MEK/toluene mixtures. The nitrile gloves are also a fairly good choice for pure toluene. One should note, however, that the manufacturers of the PVA gloves report this material to be water soluble. In accordance, they recommend it should not be used in water-based solutions. Natural rubber and nitrile rubber gloves offer limited protection from mixtures of MEK and toluene and are not recommended for operations requiring prolonged exposure to these solvents. They do provide protection, though, against splashes or other brief exposures.

Table III shows the breakthrough times of MEK and toluene through the same glove materials obtained from previous studies. These data verify the recommendation of PVA as the glove of choice with MEK and toluene. They also exemplify the significant variation in the performance of gloves made of the same material but by different manufacturers, which may be related to the different additives and preservatives added to the gloves by the manufacturers.

TABLE III
Breakthrough Times of MEK and Toluene Mixtures through Natural Rubber, Nitrile Rubber, and PVA Glove Materials Obtained from Previous Studies

	Reference	Glove material	Manufacturer	Stock no.	Reported thickness (mm)	Breakthrough time (min)	Thickness adjusted breakthrough time ^a (min/mm ²)
MEK	Nelson et al. (1981) ³	Natural rubber	Playtex	834	0.52	9.2	34
		Natural rubber	Calif. Safety	D-7-28317	0.45	8.0	40
		Natural rubber	Calif. Safety	CST-4312	0.59	16.0	46
		Nitrile	Edmont-Wilson	37-155	0.35	6.4	52
		Nitrile	Edmont-Wilson	37-175	0.37	6.0	44
	Tubby (1991) ⁷	Nitrile	Edmont-Wilson	37-185	0.55	12.0	40
		Nitrile	Renco COrp.	RN-12	0.31	3.6	37
		Natural rubber	Ansell Edmont	208	0.96	8.3	9
		Nitrile	Ansell Edmont	37-155	0.69	18.8	39
		PVA	Ansell Edmont	15-552	0.89	>6 hours	—
TOLUENE	Nelson et al. (1981) ³	Natural rubber	Playtex	834	0.52	5.0	18
		Natural rubber	Calif. Safety	D-7-28317	0.45	3.0	15
		Natural rubber	Calif. Safety	CST-4312	0.59	4.1	12
		Nitrile	Edmont-Wilson	37-155	0.35	19.0	155
		Nitrile	Edmont-Wilson	37-175	0.37	36.0	263
	Davis et al. ²⁹ (1986)	Nitrile	Edmont-Wilson	37-185	0.55	>60	>200
		Natural rubber	—	—	0.39	<15	<100
		Nitrile	—	—	0.80	30 to 45	47 to 70
	Mickelsen et al. (1986) ⁵	Nitrile	Edmont Becton	37-155	0.38	Approx. 35	Approx. 240
	Fosberg and Faniadis (1986) ⁴	PVA	Edmont	15-552	—	>4 hours	—
	Vahdat (1987) ¹² Tubby (1991) ⁷	PVA	Edmont	15-554	1.67	>20 hours	—
		Natural rubber	Ansell Edmont	208	0.96	5.6	6
		Nitrile	Ansell Edmont	37-155	0.69	62.3	131
		PVA	Ansell Edmont	15-552	0.89	>6 hours	—

^a Except for Tubby (1991),⁷ they were not provided in the papers. They were calculated from the thickness and breakthrough time given by the authors.

Although the breakthrough time must be the primary criterion with regard to personal protection, it is not the only consideration when glove selection is made. The permeation rate of the solvents should also be considered. The two parameters can be used to estimate the potential dermal exposure resulting from the use of the glove for time periods longer than the breakthrough time. Mansdorf²⁷ gives an approximate value of the skin exposure in μg :

$$E = (T_c - T_b) \times (J \times A) \quad (4)$$

where T_c is the contact period, min; T_b is the breakthrough time, min; J is the steady state of maximum permeation rate, $\mu\text{g}/(\text{cm}^2 \times \text{min})$; and A is the area of the glove material exposed to the solvent.

Table IV shows the actual dermal exposure resulting from the use of natural rubber and nitrile gloves with the five solvent mixtures. These values were obtained directly by integration of the permeation

curves for 1 h and represent the amount of the solvents that passed through the area of the glove sample. A comparison of the actual values and the exposures estimated by eq. (4) showed that the latter were consistently higher in the order of 20–75%.

Additional considerations in glove selection include tactile sense, comfort, and price. During the course of

TABLE IV
Dermal Exposure (g) Resulting from the Use of Natural Rubber and Nitrile Gloves for 1 h

	100%	75%	50%	25%	0%
Natural rubber					
MEK	100%	75%	50%	25%	0%
	0.21	0.38	0.52	0.46	—
Toluene	0%	25%	50%	75%	100%
	—	0.18	0.64	1.50	2.40
Nitrile rubber					
MEK	100%	75%	50%	25%	0%
	2.39	2.00	1.17	0.42	—
Toluene	0%	25%	50%	75%	100%
	—	0.47	0.78	0.75	0.04

these experiments, all types of gloves tested were also used for our personal protection to get a feeling of how easy it is to work with them. With regards to tactile sense, both natural rubber and nitrile performed rather well. Natural rubber, despite the fact that is almost twice as thick as nitrile (0.83 versus 0.49 mm, respectively) has a slight advantage, mainly because it is more elastic and it fits closer to the hands. With PVA gloves, tasks such as capping small vials or placing a glove piece in the permeation cell were severely obstructed. This had to do more with the glove's stiffness than its thickness (0.91 mm), which was close to natural rubber. Finally, an additional PVA disadvantage is its price, which is approximately fifteen times higher than the prices of both natural rubber and nitrile rubber gloves.

Based on the above, although PVA gloves offer superior protection from MEK and toluene mixtures, they do not provide an overall good option to the problem. As a result further research is needed in the area either to improve the tactile sense of PVA gloves or to increase the permeation resistance of natural rubber and nitrile gloves. Currently in the University of Washington and the National Technical University of Athens, and with support from two grants on nanotechnology from NSF and the Greek General Secretariat of Research and Technology, we are in the process of characterizing and developing polymeric Nano-Matrix Composites.²⁸ These studies may lead, among others in the development of nanomodified polymeric materials. In other words, polymeric materials that with the use of ceramic, metal, and other nanosize particles and/or fibers may exhibit superior properties with regards to permeation, tactile sense, and possibly price, to those of the materials studied here.

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