Original Article

Development of a simple method for determination of gas permeability resistance of whole chemical protective gloves

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Abstract

Objectives: We investigated the protection performance of whole gloves by developing a straightforward permeability resistance method and evaluating the permeation over 480 min. **Methods:** The permeation time for toluene was obtained for seven glove types according to the Japanese Industrial Standards. In addition, the permeability resistance of whole gloves was evaluated from the ratio of collected amount of toluene in the passive layered sampler attached to the inside and outside of the glove. **Results:** The permeation times of the two types of polyurethane gloves evaluated were less than 1 min each. However, the percentages of toluene that permeated through the whole gloves determined by the developed method were 32.5% and 6.8% for the thin and thick gloves, respectively, at 480 min and 71.8% and 24.1% for the thin and thick gloves, respectively, at 1,440 min. Permeation times for all three types of layered films were more than 1,440 min, but the whole glove tests showed differences of 1.7%, 3.1%, and less than 0.1% at 1,440 min. The causes of these differences were assumed to be related to variations in thickness, type of material, and differences in deposition state of the various gloves. **Conclusions:** It became possible to grasp the permeation performance throughout whole chemical resistant gloves, which could not be known only with material testing, using a straightforward permeability test method.

Keywords: chemical protective glove, layered film, passive sampler, permeation time, toluene

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Introduction

Chemical protective gloves are used in industrial environments to prevent chemicals from being absorbed through the skin. However, it is feared that chemicals can be absorbed percutaneously by penetrating the glove material or entering through the cuff of the glove. Mean-

while, it can be said that workers handling chemical substances do not have enough knowledge or awareness about the permeation of chemicals through protective gloves¹⁾.

Therefore, it is important to select chemical protective gloves that are resistant to the chemical substances being used and use them correctly to prevent health hazards due to percutaneous absorption. Test methods such as Japanese Industrial Standards (JIS) T8116-2005²⁾, the United States standard ASTM F739³⁾, and ISO6529-2013⁴⁾ are currently used to determine the permeation times for chemical substances used in gloves. However,

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these methods require complex measuring devices and do not specify parameters for more than 480 min.

In this study, a straightforward permeability resistance test method was developed for whole gloves. Layered samplers were fabricated and attached on the surface of a model hand inside and outside the gloves to analyze the permeation of chemicals. The ratio of the collected amount of chemicals outside compared to the inside of the glove was used to evaluate the performance of the protective gloves against chemical substances. Additionally, the chemical permeation for more than 480 min was also examined.

Methods

Tested chemical substance

The substance tested was toluene. The recommended allowable concentration of toluene according to the Japan Society for Occupational Health is 50 ppm (188 mg/m³)⁵⁾, and this is considered a substance that can be percutaneously absorbed. The GHS-classified reproductive toxicity is Category 1A; specific target organ toxicity (single exposure) is Category 1 (central nervous system); specific target organ toxicity (repeated exposure) is Category 1 (central nervous system, kidney, liver); the inhalation respiratory toxicity is Category 1, and the skin corrosion and irritation is Category 2, making it a highly hazardous substance⁶⁾.

Tested types of protection gloves

The gloves tested were produced with seven typical materials used in the workplace: nitrile rubber (NBR); polyethylene (PE); polyurethane A (PUR-A); and polyurethane B (PUR-B); as well as layer film A (LF-A), B (LF-B), and C (LF-C), which were made by layering film-like materials. LF-A is composed of ethylene-vinyl alcohol copolymer (EVOH) and polyethylene (PE), LF-B is composed of EVOH and nylon, and LF-C is composed of higher performance polyethylene (HPPE) layered film.

Table 1 shows the characteristics of each glove, including material, size, permeation time indicated by the manufacturer, thickness indicated by the manufacturer (mm), weight (g/m²), and surface area (cm²).

Determination of chemical resistance of protective gloves materials

The permeability resistance test of the glove material was carried out in accordance with JIS T 8030 (2015), “Protective clothing-protection against chemicals — Determination of resistance of protective clothing materials to permeation by liquids and gases”⁷⁾. Figure 1 shows an outline of the device. Three parts of one test glove were cut out to make a test piece. The test pieces were set one by one in a permeability resistance test cell and placed in a temperature constant controlled box kept at 20°C. Clean air was pumped continuously to the cell on the permeability side of the permeability resistance test at a flow rate of 350 mL/min. Approximately 70 mL of toluene was placed in the cell on the side of the test solution. A 1 mL sample of air coming out of the cell in the permeability side after 1, 20, 40, 60, 240, 480, and 1,440 min of the start of the test was injected into GC-FID 6890 GC System (Agilent Technologies, Santa Clara, CA, USA) using a gas-tight syringe and the concentration of toluene vapor was analyzed.

The normalization permeation rate, P , was determined using the following equation.

$$P = C \cdot F / A$$

Here, C is the concentration of organic solvent vapor of air coming out of the cell in the permeability side (μg/mL), F is the flow rate (350 mL/min), and A is the exposed surface area of the test cell (20.42 cm²). In the JIS standard, the time at which the normalization permeation rate in “Test of determination of resistance on protective materials to permeation by liquids using open-loop type” reaches 0.1 μg/cm²/min is defined as the normalized breakthrough detection time.

Table 1. Characteristics of tested protection gloves

Material	Indicated Permeation Time, min [†]	Measured Permeation Time, min ^{††}	12 measured thicknesses, mm				Weight, g/m ²	Surface Area, cm ²
			Max	Min	AM	SD		
NBR	Unknown	<10	0.12	0.1	0.11	0.01	74.7	658.8
PE	Unknown	<10	0.02	0.01	0.01	0.002	12.6	673.1
PUR-A	Unknown	<10	0.94	0.87	0.91	0.023	576.9	866.9
PUR-B	Unknown	<10	0.27	0.21	0.23	0.016	268.8	668.5
LF-A	>480	>1,440	0.09	0.08	0.08	0.002	78.2	1,184.1
LF-B	>480	>1,440	0.06	0.05	0.06	0.002	55.9	1,543.8
LF-C	>480	>1,440	0.08	0.08	0.08	0.001	76.2	1,158.8

AM, arithmetic mean; SD, standard deviation. (n = 3)

[†] The value indicated by the manufacturer

^{††} The value indicated by this study

Fig. 1. Diagram of testing method for chemical resistance of protective glove materials. Compress the glove material into the permeability resistance test cell. Adhere the test solution to one side of the cell, use an air compressor on the permeable side of the cell, and supply air to the dehumidifier. Gas chromatograph inspection is used to measure the test substance field in the air of the test sample out of the cell exhaust.

Fig. 2. Schematic diagram of the developed layered sampler. Toluene vapor generated by the gas generator and air are combined and adjusted to a constant gas concentration, temperature, and humidity. Subsequently, the vapor flows into the exposure cell. Test gloves equipped with a layered sampler are placed in an exposure cell and exposed to toluene vapor flowing at a constant flow rate.

Determination of permeability resistance of whole chemical protective gloves

A layered-film type passive sampler was developed to test the permeation performance of the whole gloves⁸⁾. Figure 2 shows a schematic diagram of the developed layered sampler. The sampler was based on activated carbon fibers (ACFs). Experiments were conducted to determine the effectiveness of the ACFs for absorbing toluene organic solvent vapor. The calculated sampling rate (SR) was 1.2 mL/min (4.5 ng/ppm·min). The limit of quantitation (LOQ) of toluene in the desorbed solvent was 2.00 µg/sample, which was lower than the value when 1/10 of Occupational Exposure Limits was sampled for 4 h. The recovery rates of the spike and recovery tests

were 94% or more, and the recovery rates on the 8th day of storage tests with a sampled toluene concentration of 20 ppm were 99.8% at 4°C. In the experiment on indoor environmental conditions, the collected toluene amount was constant under the following conditions: temperature of 15–30°C, relative humidity of 48–75%, and wind velocity of 0.1–0.3 m/s. The above results suggest that sampling is possible within a certain range of environmental conditions examined in this study. Layered samplers were attached on the surface of a model hand and outside the gloves in a slightly offset position. The protective performance of the gloves against vaporous chemical substances was evaluated based on the ratio between the amount of chemicals inside and outside the glove.

Figure 3 shows a structural diagram of the test device. Figure 4 shows the photograph of the exposure cell. The sleeves of the gloves attached to the test equipment were sealed.

Assuming that the protective gloves were exposed to toluene vapor at actual work sites, test gases, adjusted to a toluene concentration of 50 ppm, a temperature of 25°C, and a humidity of 40%, were injected into the exposure cell containing the gloves. ACF pieces in the sampler where the amount of toluene was collected at 240 and 480 min (or 480 and 1,440 min) from the start of experiments were placed into a vial. The samples were then analyzed with a combined gas chromatograph-flame ionization detector (GC-FID) after 2.0 mL of carbon disulfide was added and desorbed. The permeation ratio was determined as the amount of toluene collected inside the glove divided by the amount of toluene collected outside the glove (in %) and its criterion was 0.1%. The tests were carried out three times each, and the arithmetic mean value was obtained.

Fig. 3. Diagram of experimental device for permeability resistance analysis of whole chemical protective gloves. A layered sampler is attached to the surface of the hand model, after which the hand model is placed in the test gloves and sealed. Subsequently, the hand model is placed inside the exposure cell. Toluene vapor enters through the inlet of the exposure cell and exits through the outlet.

Fig. 4. Photo of the exposure cell used for the permeability resistance experiment of whole gloves

Analytical method of toluene

Toluene was quantitatively analyzed using a GC-FID 6890 fitted with an autosampler 18593B (Agilent Technologies, Santa Clara, CA, USA). The columns used were DB-WAX 30-m-long, inner diameter 0.32 mm, cross-linked polyethylene film thickness 0.5 μm (Agilent Technologies, Santa Clara, CA, USA) and with an automatic liquid sample injector (7683 Series Injector; Agilent Technologies, Santa Clara, CA, USA). Column temperature conditions were as follows: held at 40°C for 3 min and then raised to 200°C at 10°C/min. The detector temperature was 200°C, the inlet temperature was 180°C, and the sample liquid introduction amount was 1 μL .

Results

Protection test for chemical resistance of protective gloves materials

Table 1 shows the results of thicknesses, weight, surface area, and permeability resistance tests for toluene

conducted on seven types of glove materials. In addition, the average glove thickness measurement ($n=3$) was 0.10 mm at the base of the nitrile rubber finger, and 0.12 mm at the tip. The PUR-A had a palm back of 0.94 mm, a thumb base of 0.91 mm, an index finger base of 0.89 mm, and a ring finger base of 0.90 mm.

The normalization permeation rates of NBR, PE, PUR-A, and PUR-B reached 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ within 10 min after the start of all three tests. In comparison, the normalization permeation rates of LF-A, LF-B, and LF-C did not reach 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$, even with a permeation time over 1,440 min.

Permeability resistance test of glove materials: determination of permeability resistance of whole chemical protective gloves

Table 2 shows the toluene ratio from inside the passive sampler relative to the outside surface over time. Results of permeation ratio of glove showed that among the seven glove types, PE had obtained the highest permeation ratio in the shortest time, with 57.3% and 72.8% permeation ratios after 240 and 480 min, respectively. This increase was faster than the 10.2% and 14.6% values obtained in the period for NBR. As for PUR-A, permeation was 6.8% and 24.1% at 480 and 1,440 min, respectively, whereas PUR-B had 32.5% and 71.8% permeation ratios at 480 and 1,440 min, respectively. In comparison, LF-A, LF-B, and LF-C had <0.1% even after 480 min. However, LF-A and LF-C had a permeation ratio of 1.7% and 3.1%, respectively, at 1,440 min. Furthermore, the relative standard deviations of PUR-A and PUR-B tested thrice were as high as 21.2% and 30.9%, respectively, at 480 min and 46.8% and 7.5%, respectively, at 1,440 min. From the above, favorable results were obtained in these experimental conditions only for LF-B, with permeation ratio of less than 0.1 even after 1,440 min of exposure.

Table 2. Permeability resistance results of whole chemical protective gloves

Material	Exposed time, min	Permeation ratio, [†] %			AM	SD	RSD
NBR	240	10.3	8.1	12.0	10.2	1.6	15.7
	480	14.0	14.6	15.3	14.6	0.5	3.7
PE	240	57.6	54.0	60.2	57.3	2.5	4.4
	480	69.2	73.5	75.6	72.8	2.7	3.7
PUR-A	480	6.0	5.6	8.9	6.8	1.5	21.2
	1,440	38.6	22.6	11.1	24.1	11.3	46.8
	480	21.3	45.7	30.5	32.5	10.1	30.9
PUR-B	1,440	67.3	79.3	68.8	71.8	5.4	7.5
	480	<0.1	<0.1	<0.1	<0.1	0.0	0.0
LF-A	1,440	0.1	4.9	<0.1	1.7	2.3	137.9
	480	<0.1	<0.1	<0.1	<0.1	0.0	0.0
LF-B	1,440	<0.1	<0.1	<0.1	<0.1	0.0	0.0
	480	<0.1	<0.1	<0.1	<0.1	0.0	0.0
LF-C	480	<0.1	<0.1	<0.1	<0.1	0.0	0.0
	1,440	2.6	2.8	4.0	3.1	0.6	19.4

AM, arithmetic mean; RSD, relative standard deviation; SD, standard deviation. (n=3)

[†] Permeation ratio: ratio of collected amount of inside to collected amount of outside

Discussion

NBR, PE, PUR-A, and PUR-B reached normalization permeation rates of 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ in less than 1 min, which was a very short time after the start of the test; no clear differences were observed in the permeation times. LF-A, LF-B, and LF-C also had permeation times of more than 1,440 min according to the permeability resistance test of glove materials based on the JIS method. However, it was observed that LF-A and LF-C took 480 min, whereas LF-B took over 1,440 min based on the results of the whole glove permeability tests. Comparing the concentration ratios of the inside and outside of the glove by performing the permeability test, it was possible to analyze the permeability of a whole glove with a realistic shape and size.

Necessity in determining the chemical resistance of protective gloves to permeation by gases

The permeability resistance test was adopted to evaluate the effectiveness of the chemical protective gloves and clothing due to a revision in the JIS in June 1998. The penetration test and degradation test examine changes, such as expansion, contraction, and hardening; tensile strength and expansion coefficient are determined by repeatedly passing the liquid through the connection and immersing the finished product. Meanwhile, the permeation test investigates the phenomenon in which a chemical substance is absorbed by the surface of a material, is diffused at a molecular level, and is detached from the backside of the material. Miyauchi et al. conducted a permeation test for 14 types of chemical substances in liquid contact with 10 types of protective gloves and compared their results with those of the degeneration test shown by

the manufacturer. Results showed that of the 51 combinations that were indicated as usable in the permeation test results, 17 had a permeation test value of under 30 min, corresponding to 33% of the total. Even if the results were favorable enough to be used in the penetration test indicated by the manufacturer, some were inconsistent with the obtained results. Therefore, vaporous chemicals could penetrate and reach the skin even if there was degradation resistance. Considering the prevention of exposure during actual use, it is crucial to consider the permeability resistance test results when selecting chemical protective gloves.

JIS T8116 specifies a permeation test method for permeability performance. However, this test is carried out by cutting out the material used; this does not properly address the permeability performance of the entire product, which considers permeability between the sections of the glove in contact with the body, connections between the main body and glove, and differences in the thickness of the glove material.

As a test method capable of evaluating the permeation resistance performance of the whole product, Miyauchi et al. prototyped experimental equipment to evaluate the permeability resistance performance of whole gloves and boots in which the test liquid and glove material come into contact and reported test results with various organic solvents¹⁰⁾. For dichloromethane, permeability resistance test results of the whole glove showed relatively shorter permeation times, with a measured value of 8 min relative to the permeation time of 20 min given by the manufacturer for the multi-layer film glove (n=3), 9 min relative to 12 min given by the manufacturer for butyl rubber, and 48 min relative to the 92 min given by the manufacturer for fluorocarbon rubber. It is presumed that the cause was

the permeation of the glove material at the attached part and connections and differences in thickness depending on the glove part.

Airek et al. prototyped a permeability resistance test device of a whole glove where a test liquid and the glove material come into contact; a robot arm was used to test a hand grasping state¹¹⁾. Experiments examining the permeation state of cyclohexanol when a robot with nitrile gloves was grasping an item showed further permeation of cyclohexanol. Xu et al. also prototyped a full permeability resistance test device for latex gloves in metalworking fluid and determined the permeation amount into the glove per unit time, showing that this permeation amount was higher than when using the method where the material was cut out according to ASTM¹²⁾. These experiments were performed in liquid target substances, so although they differed from the vaporous target substances in this study, their experiments were also different from the tests where the material was cut out. Therefore, to accurately ascertain and prevent exposure of chemical substances on the hand's surface inside gloves in real conditions, permeability resistance tests of whole gloves are necessary.

Determination of permeability resistance of whole chemical protective gloves

Measurement results showed that of the seven types of gloves, the average permeation time for the material was less than 10 min for NBR, PE, PUR-A, and PUR-B. However, with regard to the glove internal/external collection amount ratio, PE reached the highest internal/external collection amount ratio within the shortest time, with average values of 57.3% and 72.8% at 240 and 480 min, respectively. PUR-A had values of 6.8% and 24.1% at 480 and 1,440 min, respectively, whereas PUR-B had higher values of 32.5% and 71.8% at 480 and 1,440 min, respectively.

One of the causes for differences according to type, even in the same material (polyurethane for example), was that the average thickness of each part of PUR-B was 0.21 (standard deviation, 0.016) mm, whereas PUR-A was 0.93 (standard deviation, 0.023) mm; differences in permeation are considered to be largely related to material thickness. Erja et al. conducted EN 374¹³⁾ and ASTM F739¹⁴⁾ tests for the permeability of isopropyl alcohol in six types of natural rubber and chloroprene rubber and showed that the permeation time was longer with increased thickness in any of the test methods in the case of the natural rubber material¹⁵⁾.

In addition, relative standard deviations (RSD) of the internal/external concentration ratio of PUR-A measurements ($n=3$) were 21.2% and 46.8% at 480 and 1,440 min, respectively; whereas those for PUR-B were 30.9% and 7.5%, respectively, with large variations observed (Table 2). The measurement results of glove thickness showed that the PUR-A thickness tended to exhibit thin-

ner values for the palm relative to the back, as well as the base of the thumb, index finger, and ring finger relative to their tips. Differences in thickness by location were particularly pronounced for the polyurethane gloves, and it was estimated that this was one of the causes for the variation in the internal/external collection ratio. It can be said that this is a new finding that could not be determined only by the material testing of gloves.

About LF-A, LF-B, and LF-C results

Meanwhile, Bensel evaluated the working speed of bare hands and chemical protective gloves with three thicknesses of 0.18, 0.36, and 0.64 mm. It was then found that bare hands had the fastest working time and the 0.64 mm gloves had the slowest time¹⁶⁾. While permeation time can be improved by increasing the thickness, the working time also is affected, subsequently increasing the contact time with the chemical substance.

Well et al. measured the effort required and the electric activity of the forearm muscles with gloves of different sizes and thicknesses, and results showed that thicker gloves decreased performance, increased effort and electromyographic amplitude, and decreased self-evaluated comfort/fit/workability¹⁷⁾. Increasing the thickness of gloves increased the workload and caused a decrease in workability; therefore, it is important to select gloves both in terms of confirming workability and the permeability resistance test.

The thicknesses of LF-A, LF-B, and LF-C were 0.1 mm or less, which were thinner than other products, and it was estimated to be relatively favorable in terms of workability. The permeability resistance performances of all the glove materials were over 1,440 min. Meanwhile, the internal/external collection ratio conducted with the entire glove at 1,440 min was 1.7% for LF-A, 3.1% for LF-C, and less than 0.1% for LF-B; this was deemed to be one of the causes of very little leakage from the attached part. As a result of conducting the entire glove tests, we consider that continuous use of LF-A and LF-C for 1,440 min was unsuitable but that LF-B could be used continuously for over 1,440 min.

Present situation and problems

ASTM and ISO require that the penetration test and permeability resistance test are conducted^{3,4)}. In Japan, JIS was revised in 1998, and the permeability resistance test was added¹⁸⁾.

A notification from the Ministry of Health, Labour and Welfare also stated the following: "Chemical protective gloves should have a margin for work by referring to the permeability class and other scientific justifications listed in the instruction manual of the chemical protective gloves". The gloves should be used within the time to reach permeation rate 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$. The following was also stated regarding the management of chemical protec-

tive gloves at worksites: “The employer shall appoint a personal protective equipment manager who manages chemical protective gloves at each worksite from among those who have the knowledge and experience concerning industrial health (e.g., health manager, operation chief). Workers should be instructed on the proper selection, wearing, and handling of chemical protective gloves and they should be in charge of the proper maintenance and management of chemical protective gloves”¹⁹⁾.

In response, Kabe et al. reported a fact-finding survey on the selection, wear, and maintenance of chemical protective gloves at business sites in Japan¹⁾. Questionnaire results of 817 workers who use chemical protective gloves and their managers and supervisors at the workplace show that 46.1% and 43.2% knew about the “types and features of chemical protective gloves” and “degradation, penetration, and permeation of chemical protective gloves”, respectively. Among these, 27.7% of supervisors and 41.2% of field workers answered that “the permeability test results of the target substance are obtained” from the “selection” survey results, with field workers comprising a significantly higher share ($p=0.022$). However, both groups had low awareness, at less than 50%. For the “how to use” section, 34.1% of supervisors and 48.5% of field workers answered that “the storage period was confirmed before starting work”, with similar fractions for both. From these results, both supervisors and field workers had difficulty correctly evaluating the performance of chemical protective gloves and using them correctly.

The management supervisors, in particular, are expected to be in a position to instruct field workers by improving their awareness of chemical protective gloves and understanding of how to use them. The management supervisor is required to provide detailed guidance and knowledge regarding the gloves to be used according to the actual conditions of use; it is also necessary to set clear criteria for when to replace the chemical protective gloves according to the actual conditions. Chemical protection gloves with particularly good performance tend to be expensive; this simple measurement method, which does not require complicated devices, can promote correct selection, including rational replacement time.

Conclusions

By developing a simple permeability resistance test method of whole chemical protective gloves using the layered samplers, it became possible to evaluate the permeation status of the whole glove, information that was unknown when only the material test was conducted. Given that the thickness differs depending on the part of the glove, it can be said that it is necessary to consider the actual usable time, including the result of the entire test. However, this study only included three repeated measurements, and more repetitions are advised. Seven

types of gloves were targeted, and toluene was the only tested substance. Considering the use of gloves in real conditions, it is necessary to investigate more types of gloves and test substances. It is also desirable to carry out internal/external ratio measurements when chemical substances are being handled in an actual work site instead of just exposure conditions with a fixed concentration using an experimental device. Last but not least, it is important to promote rational chemical substance management based on this research.

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Conflict of interest

The authors have no conflicts of interest directly relevant to the content of this article.

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