〔Original〕

Examination of Permeation Resistance of Chemical Protective Gloves Made of Laminate-Film Materials Against Chemical Substances

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Abstract **:** This study investigated the permeation resistance of chemical protective gloves made of laminate film comprising nylon, ethylene-vinyl alcohol copolymer (EVOH), and other materials against different chemical substances to examine their usability in different work processes. The permeation resistance of the chemical protective glove was tested using the Japanese Industrial Standards (JIS) test method against twelve substances: acetone, acetonitrile, dichloromethane, ethyl acetate, n-hexane, methanol, tetrahydrofuran, toluene, 2-propanol, 1-butanol, 1,4-diethylene dioxide, and ethanol. After 480 min, no substance, except for methanol and ethanol, permeated at a standard permeation rate of 0.1 $\mu g/cm^2/min$. Methanol and ethanol showed permeation at 1 min and 30 min elapsed, respectively. Hence, the gloves tested in this study exhibited permeation resistance to various chemical substances, and can thus be used in many work processes. Some film materials have short permeation time against certain chemical substances, but the chemical protective gloves tested in this study can be used at work sites, such as manufacturing sites, that require permeation resistance to different chemical substances.

Keywords **:** chemical protective glove, laminate film, permeation resistance, organic solvent.

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Introduction

In 1970, before the enactment of Japan's Occupational Safety and Health Law, the number of occupational accidents resulting in four or more days of absence from work due to exposure to chemical substances was 1,254; in contrast, after the law was enacted, the number declined steadily, reaching 587 in 1980 [1]. The rate of this decrease began to diminish by 1985, however, and the number of accidents leveled off in 1986. Because of the limitations of substance-specific legislation, the Chemicals Risk Assessment was introduced in light of the situation where tens of thousands of chemicals were available on the market. As a result, the number of occupational accidents decreased to 244 in 2009; however, this decline ended in 2010 [2].

Skin problems resulting from exposure to chemical substances account for over half of the chemical substance-related health disorders leading to more than four days of absence from work [3], and several occupational fatalities presumably caused by the transdermal absorption of chemical substances have been reported by the Ministry of Health, Labour and Wel-

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fare of Japan [4]. Based on these circumstances, the Ministry of Health, Labour, and Welfare revised the Ordinance on Industrial Safety and Health in 2023. As per the new Article 594-2, "Employers must ensure that employees use appropriate protective equipment, such as impermeable protective clothing, protective gloves, footwear, and safety glasses when engaged in work involving manufacturing or handling of chemical substances that could potentially damage the skin or eyes or cause health disturbances by being absorbed through or penetrating the skin" [5]. When choosing chemical protective gloves, those that have permeation resistance against chemical substances used must be considered [6].

Numerous chemical substances are used at work sites, usually in a single day, thus requiring selecting and replacing appropriate chemical protective gloves for each work process, which is challenging and cumbersome. Therefore, chemical protective gloves that can be used against all different chemical substances for different work processes must be developed. In recent years, chemical protective gloves with permeation resistance against different chemical substances have been developed using laminate films made of multiple materials.

Among previously developed chemical protective gloves, those made of multilayer film incorporating ethylene-vinyl alcohol copolymer (EVOH) have attracted attention for their effective protective properties [7]. Although specific permeability test data have been published by various manufacturers, key information such as detailed permeability test methods and data on reproducibility has not been published.

In this study we investigated the chemical permeation resistance of chemical protective gloves developed using laminated films consisting of nylon, EVOH, and other materials [8]. The structure of the studied multilayer films, permeation resistance test method, and test conditions are described, and the relationships between test results are clarified.

Materials and Methods

Examined Chemical Substances

Eight organic solvents (acetone, acetonitrile, dichloromethane, ethyl acetate, n-hexane, methanol, tetrahydrofuran, and toluene) were selected among the substances recommended for permeation resistance testing of chemical protective clothing/protective clothing materials in Appendix A of the Japanese Industrial Standards (JIS) T8030, which specifies the resistance testing method for chemical protective gloves [9]. Four general-purpose solvents (isopropyl alcohol, 1-butanol, 1,4-dioxane, and ethanol) were also tested, thus resulting in a total of 12 test substances. Because most organic solvents are used in mixtures in actual workplaces, this study examined glove materials that are permeable to a wide variety of organic solvents. The chemical protective glove tested in this study was made of a 60-μm thick five-layer laminate film comprised of nylon, EVOH, modified polyethylene, and linear low density polyethylene (L-LDPE) (Figure 1). The structure of the laminate film is shown in Figure 2.

Figure 1. Chemical protective glove tested in this study.

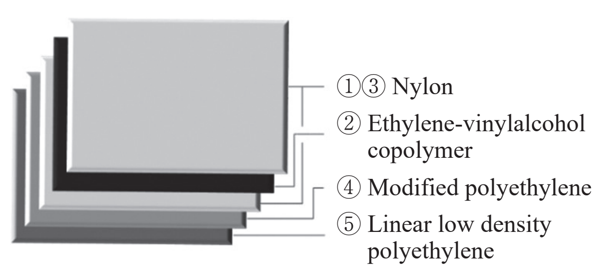

Figure 2. Structure of the multilayer laminate film constituting the chemical protective glove.

Permeation Resistance Test

We tested the permeation resistance of the chemical protective glove according to the permeation test method of the JIS T8030 open circuit system [9]. Figures 3 and 4 show the schematics of the permeation resistance test and permeation resistance test cell, respectively. The permeation resistance test cell was installed inside an exhaust system in a room maintained at a room temperature of 22°C (±1.5°C). Three test pieces were cut out from the part of the glove corresponding to the back of the hand (sample numbers 1−3). For the test, a test piece was placed in the permeation resistance test cell fixed with bolts to act as a partition wall. Next, 70 m*l* of a test chemical substance was added to one side of the permeation resistance test cell and brought into contact with the entire surface of the test piece. Air purified through the silica gel and activated carbon was continuously pumped at a flow rate of 350 m*l*/min into the other side of the cell.

After 480 min from the time of contact between

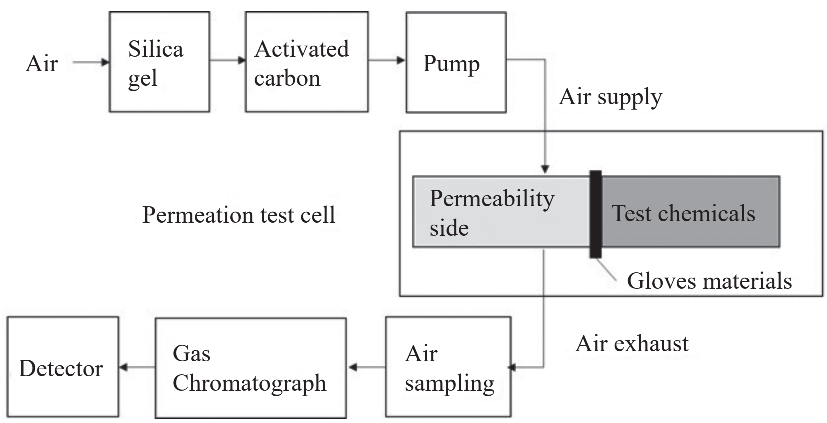

Figure 3. Schematic of the permeation resistance test. The air, from which water vapor and organic gases have been removed using silica gel and activated carbon, is continuously supplied to the permeation test cell by a pump at 350 m*l*/min. The supplied air is mixed with the test solvent gas permeated from the glove materials at the permeability side in the permeation test cell and discharged. The discharged air is collected at 1 m*l*, introduced into a gas chromatograph, separated, and quantified using an FID detector. FID: Flame Ionization Detector.

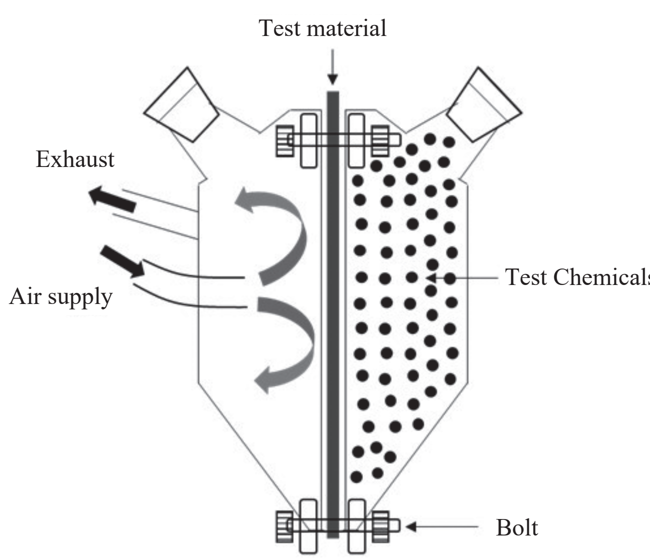

Figure 4. Schematic of the permeation-resistance test cell. The permeation-resistance test cell is bolted together with the test material in between. One side of the test cell, which is divided into two parts by the test material, is filled with the test chemical, and the test chemical gas that permeates through the test material is mixed with a continuous supply of air and discharged.

the chemical substance and the test piece, 1 m*l* of the air exhausted from the test cell was collected using a gas-tight syringe. To determine the total amount of permeated chemical substance, the collected air was introduced into the gas chromatography system Nexis GC-2030 FID (Shimadzu Corporation). The time to reach the standard permeation rate of 0.1 μg/cm^2/min, specified by JIS T8116, was defined as the permeation time [10]. The permeation rate P was determined as

$$P = C \cdot F / A \qquad (1)$$

where C is the vapor concentration of the chemical substance in the exhaust air exiting the test cell (μg/m*l*); F is the flow rate (350 m*l*/min); and A is the contact surface area between the chemical substance and the test piece in the test cell (20.42 cm^2).

Owing to the possible early permeation of alcohols (methanol, 1-butanol, 2-propanol, and ethanol) through EVOH, the exhaust air was collected at 1, 10, 20, 30, 60, 240, and 480 min after the time of contact to determine the permeation rate. The test was terminated when the permeation rate reached the standard rate of 0.1 μg/cm^2/min.

Results

Table 1 summarizes the results of the permeation. After 480 min, none of the tested substances, except methanol, exhibited permeation reaching the standard rate of 0.1 μg/cm^2/min; furthermore, their permeation time exceeded 480 min. Conversely, after 1 min, the permeation of methanol reached the standard rate of 0.1 μg/cm^2/min, and its permeation time was below 1 min.

Discussion

The characteristics of the EVOH Inside the Layer of Laminate Film

Our results indicated that the chemical protective glove made of laminate film had the capacity for permeation resistance against all the tested organic solvents except methanol, thus suggesting the possibility that one type of glove can be used in various work processes. The permeation resistance capacity against various organic solvents, such as oxygen and organic solvents, can be attributed to the characteristics of EVOH, a synthetic resin film first developed by Kuraray Co., Ltd. in 1972 [7].

Table 1. Results of the permeation test of the chemical substances

	Permeation time (min)*		
Chemical substances	Sample 1	Sample 2	Sample 3
toluene	>480	>480	>480
acetone	>480	>480	>480
etyl acetate	>480	>480	>480
tetrahydrofuran	>480	>480	>480
methanol	<1	<1	<1
acetonitrile	>480	>480	>480
dichloromethane	>480	>480	>480
1,4-diethylene dioxide	>480	>480	>480
1-butanol	>480	>480	>480
2-propanol	>480	>480	>480
n-hexane	>480	>480	>480
ethanol	<30	<30	<30

*Permeation time is the time when the standard transmission rate of 0.1 μg/cm^2/min is reached. A maximum of 480 min was observed.

The amount of gas permeation in a polymer (cc(stp)/m^2 · d · atm) is inversely proportional to the thickness, which is expressed as:

$$Q = P \cdot (P1 - P2) \cdot A \cdot t / l$$
$$D \cdot S \cdot (P1 - P2) \cdot A \cdot t / l \qquad (2)$$

where Q is the amount of permeation; P is the permeation coefficient; P1 is the gas pressure on the high-pressure side; P2 is the gas pressure on the low-pressure side; A is the area of the film; t is time; L is the thickness of the film; D is the diffusion coefficient; and S is the solubility coefficient. Increasing the thickness improves permeation resistance capacity but reduces operability, thereby increasing work fatigue [11].

Additionally, the permeation coefficient (P) increases as the temperature increases (Equation 3).

$$P = K \cdot \exp(-E / R \cdot T) \qquad (3)$$

where K is a constant; E is the activation energy; R is the gas constant; and T is the absolute temperature. The amount of permeation through EVOH increases as the temperature increases, although it varies depending on ethylene content [12].

The permeation resistance capacity of EVOH against oxygen decreases at high relative humidity [13−17] as water molecules bond with hydroxyl groups of EVOH, which lowers the glass transition temperature (Tg) and over-plasticizes the polymer [18]. This decrease is limited, however, when EVOH is used as the intermediate layer of the film [19]. Regarding the chemical protective glove tested in this study, the effects of temperature and relative humidity were likely suppressed, considering that EVOH was sandwiched by two layers of nylon. Various types of nylon can be synthesized using different methods [20]. For example, nylon 6, produced by polymerization of ε-caprolactam, is highly hygroscopic and strong. Nylon 66, produced by polycondensation of hexamethylenediamine and adipic acid, has lower hygroscopicity and higher elastic modulus than nylon 6. Nylon 11, which is produced by polycondensation of ω-aminoundecanoic acid, and nylon 12, which is produced by ring-opening polymerization of ω-laurolactam or polycondensation of aminododecanoic acid, have lower hygroscopicity than other types of nylon. Similarly, the nylon in the laminate film in this study likely had low hygroscopicity.

Comparison of Permeation Resistance to Oxygen and Organic Solvents

We examined whether the oxygen permeation resistance corresponds to the permeation resistance against organic solvents in polyvinyl alcohol (PVA), EVOH, and polyvinyl chloride (PVC). Kariya stated that PVA exhibits the highest oxygen permeation resistance (m*l*/m^2·24H·atm), followed by EVOH33mol% and PVC, respectively [21]. Regarding organic solvents, Miyauchi *et al* showed that EVOH exhibited the highest permeation resistance against acetone and carbon disulfide, followed by PVA and PVC, which had comparable permeation resistance [22]. The permeation resistance against trichloroethylene was the highest in EVOH, followed by PVC and PVA. The permeation resistance against N,N-dimethylformamide was the highest in EVOH, followed by PVA and PVC. This indicates that oxygen permeation resistance does not necessarily correspond to permeation resistance against organic solvents. This can likely be attributed to the high solubility of the film surface because the permeation phenomenon occurs when the permeating substance comes into contact with the film surface, resulting in dissolution of the film surface, diffusion of the substance into the film, and detachment of the substance from the back of the film.

Permeation Resistance to Alcohols

Methanol and ethanol had short permeation times, below 1 min and 30 min, respectively, so attention should be paid to their usage time. In particular, we found that the chemical protective glove tested in this study must not be used in work that involves methanol since EVOH is generally produced by saponification of ethylene-vinyl ester copolymers, which are obtained by copolymerizing ethylene and fatty acid vinyl ester under a high temperature and high pressure in the presence of an alkali catalyst using alcohol as a solvent, such as methanol. Methanol was presumed to be used as a solvent for purification and saponification of ethylene-vinyl ester copolymers. This indicates that the EVOH film used in this study was dissolved particularly by methanol due to its affinity, thereby enlarging the molecular gaps between the polymer chains in the film and allowing methanol gas to permeate. Conversely, ethanol had a permeation resistance time of below 30 min, whereas the permeation resistance time of 1-butanol and 2-propanol exceeded 480 min. Then, the EVOH alcohol solution obtained from the abovementioned saponification process was converted into a water/alcohol solution of EVOH, extruded into a low-temperature coagulation bath comprising water, precipitated, and produced. Alcohols with a larger carbon number have a smaller proportion of hydrophilic groups even if they are the same alcohols. Therefore, unlike methanol, which has a large proportion of hydrophilic groups, substances with a smaller proportion of hydrophilic groups in this study may have maintained tight molecular gaps between the polymer chains, thus resulting in lower permeation than methanol (Table 2).

Chemical Protective Gloves Made of Laminate-film Materials

Table 3 presents the permeation resistance time of the chemical protective glove tested in this study and those made of other laminate-film materials (published by the manufacturers): A (polyethylene + EVOH), B (nylon + EVOH), and C (polyethylene + EVOH). The chemical protective gloves made using the laminate

Table 2. Carbon number and permeation resistance time of alcohols tested in this study

Chemical substances	Carbon number	Chemical formula	Permeation time (min)*
methanol	1	CH_4O	<1
ethanol	2	C_2H_6O	<30
2-propanol	3	C_3H_8O	>480
1-butanol	4	$C_4H_{10}O$	>480

*The average of the three permeation times for the chemical concerned reported in Table 1.

film exhibited permeation resistance against various chemical substances. Glove B had a permeation resistance time of 10 min against methanol, to which the glove tested in this study had low permeation resistance. This indicates that B cannot withstand long-term work, similar to the glove tested in this study. Conversely, A and C had permeation resistance times of 360 min and 480 min, respectively, which indicates their ability to withstand long-term work. The chemical protective gloves tested in this study and B are made of nylon, whereas A and C are made of polyethylene. Therefore, the permeation resistance capacity was likely influenced by the difference in laminating materials and the manufacturing method of the materials. There was also a large discrepancy between the tested material and B in ethanol. According to data published by EVOH manufacturers, a change in ethylene content (mol%) from 27 to 48 causes a 37-fold change in permeability (oxygen), from 0.1 to 3.7 [7]. Kim *et al* investigated the oxygen barrier and mechanical properties of PK/EVOH blend films under dry and wet conditions and found that the films exhibited a very low oxygen transmission coefficient of 0.3 to 0.16 cc 20 μmm^{-2} day^{-1} atm^{-1} as the EVOH content increased from 30 to 70 wt% [23]. Even with blended materials, the transmission coefficient varies depending on the EVOH content in the film material. Although the ethylene content of the tested EVOH and the EVOH blend state are unknown, it is assumed that this is one of the reasons for the deviation in ethanol permeation resistance.

Kabe *et al* conducted a questionnaire survey regarding chemical protective gloves with 817 individuals at seven manufacturing work sites in Japan. Only 25.2% and 29.2% of the respondents answered "I obtain the results of permeation tests for the substances used" and "I select mixed substances in consideration of short permeation time," respectively. This indicates that there is a low awareness of the procedure of "checking the permeation test results" for the substances used [24]. With the development of the manufacturing industry, a wide range of mixed chemical substances and materials will be used; therefore, chemical protective gloves that have permeation resistance against a variety of chemical substances must be developed and studied.

Table 3. Comparison of permeation resistance time of the chemical protective glove tested in this study and those made of other laminate-film materials

	Permeation time (min)			
Chemical substances	Test glove	A	B	C
toluene	>480	>480	>480	>480
acetone	>480	>1440	>480	>480
etyl acetate	>480	−	>480	>480
tetrahydrofuran	>480	>480	>480	>480
methanol	<1	360	10	>480
acetonitrile	>480	>480	>480	>480
dichloromethane	>480	>648	>480	20
1,4-diethylene dioxide	>480	>480	>480	>480
1-butanol	>480	−	<10	>480
2-propanol	>480	−	<10	>480
n-hexan	>480	>1440	>480	>480
ethanol	<30	−	>480	−

Conclusion

The results of this study indicate that the chemical protective glove using EVOH inside the layer of laminate film had permeation resistance to various chemical substances, and can therefore be used in many work processes. Although some film materials have a shorter permeation time against certain chemical substances, the chemical protective glove tested in this study will be useful at work sites that require permeation resistance to different chemical substances, such as manufacturing sites. On the other hand, only a limited number of chemical substances were examined in this study; the permeation resistance of the glove against additional chemical substances has to be tested.

Conflict of Interest

None

Financial Disclosure

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