

Study on a Novel Material Technology for Chemical/Biological Protection

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Abstract

A novel chemical/biological (CB) protective material was studied in this paper. The material was designed to provide protective properties and satisfactory wearing comfort. In the fabric construction, a PET fabric was laminated with modified PTFE membrane by paste dot coating, and then coated by PU solution in a direct process. Finally, it was laminated with active carbon felt. The modified PTFE membrane completely prevents permeation of the mustard liquid and biological warfare agent, any residuals penetrating the PU will be absorbed by active carbon felt. Furthermore, the CB protective material can provide satisfactory wearing comfort.

Keywords

PTFE membrane, modification, CB protection, PU coating

Introduction

CB protective materials have been developed that protect against liquid, vapor, and aerosol CB warfare agents. Till now, the CB protective materials are classified as impermeable, permeable, permeable absorptive and engineered permeable materials [1-4]. The impermeable materials, for example, butyl-rubber, have good protective properties, but do not allow vapors to pass through. The protective properties of permeable materials, such as traditional textiles in combination with treatment and finishing, are unsatisfactory. The permeable absorptive materials, for example, active carbon, provide protection from vapor-phase contaminants by trapping vapors as they pass through the fabric. However, these materials do not protect as well against aerosols and liquids. The engineered permeable materials have been specifically engineered to restrict the penetration of toxic contaminants

through the material but still allow water vapor transmission for personal comfort.

The latest research shows that the protective material must protect the wearer against CB warfare agents, provide satisfactory wearing comfort and support thermo-regulation processes of the human body. In order to enable protective material to fulfill the purpose completely, this selectively permeable membrane-based fabric system for CB/environmental protection has been developed in recent years. An expanded PTFE membrane[5,6] is a typical example, which has high moisture vapor transport and evaporative cooling potential, is also flexible, durable, thin, waterproof, lightweight, launderable, and low-cost. Owing to the micropores of PTFE membrane, laminated fabric enables transportation of sweat in the form of vapour, from the under-clothing space to the outside, thus establishing equilibrium between the body of the user and the environment[1].

In the foregoing studies[7,8], the PTFE membrane served as the key protective material against the Severe Acute Respiratory Syndrome (SARS). The garments were worn by the medical staff in several hospitals in China during May and June, 2003, without a single infection of medical personnel with SARS.

In this article, a novel technique of combining the permeable absorptive material, an active carbon felt and an engineered permeable material (modified PTFE membrane for CB protection) is developed.

EXPERIMENTAL

Preparation of PTFE membrane

Expanded PTFE powder produced by emulsion polymerization (CD123, Asahi Fluoropolymers Co.) was mixed with

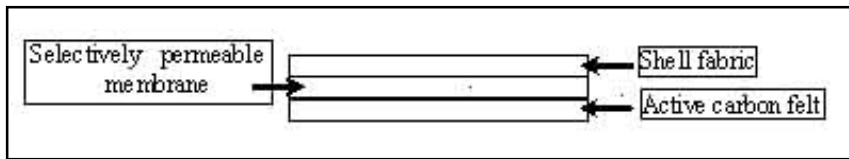


Figure 1
THE SKETCH OF CB PROTECTIVE MATERIAL

naphtha as a lubricant (20%) and then extruded into a rod of 13mm in diameter by use of an extruder. Thereafter, this rod was rolled between two metal rollers to a sheet with thickness of 120 μ m. The rolled sheet was longitudinally stretched between rollers in an oven at 200°C, while the naphtha was being driven off, thereby forming the PTFE base sheet in this study. The PTFE base sheet was then traverse stretched. Finally, to keep dimensional stability, this membrane was heated for several seconds on a stainless steel smooth roller.

Modification of PTFE membrane for improving protection

In order to improve CB protection, the PTFE membrane was treated with a surface active agent (commercial fluorochemical suspension) by padding with a 55% wet pick-up (WPU) followed by drying and curing at a temperature of 170°C for 2 min, resulting in a dry add-on of 1.55% on the weight of the film, thereby enhancing the membrane's super-hydrophobic property

Preparation of laminated fabric

A base PET twill weave fabric was selected with the following specifications: polyester filament (83dt/48f) with conductive nylon 6 filament at 1cm intervals, a weight of 90 g/m², warp number of 152 yarns per inch, weft number of 94 yarns per inch. The fabric was treated with a commercial fluorochemical finish padding with a 65% WPU and dried at 150°C for 3 min with a dry add-on of 2.56% on the weight of the fabric. A similar weight satin weave fabric made of similar yarns was also selected as the base fabric for some of the composites. The fabrics were then laminated with modified PTFE membrane by paste dot coating of thermoplastic PU polymer, and fused with heated contact rollers at a temperature of 150°C for 60 seconds. It was then coated by a solvent-based PU solution (made by the Quartermaster Research Institute of the General Logistic Department of CPLA, Beijing) and dried in an oven for 130°C for 1 min. In the final step, the PET fabric/PTFE structure was laid over with an active carbon felt without bonding (shown in Fig.1). The active carbon felt had a weight of 100 g/m² and a thickness of 2.0 mm, and the active fiber BET was 1400 m²/g.

CHARACTERIZATION

Water vapor permeability (WVP)

The WVP was measured according to GB/T 12704-91 (The value divided by 24 corresponds to that of ASTM E96 Procedure B).

A circular sample is placed into a small vessel containing a desiccant such as silica gel. The sample is conditioned at 23°C and 60% R.H. overnight. The next morning, the silica gel is

removed and replaced by fresh silica gel. After weighing the vessel, the absorbency of water vapor from the standardized surrounding air is measured by weighing it after 8h. The weight gain is multiplied by 3 and divided by the area of the testing vessel which has a constant size. The resulting value is a water vapor permeability measured as

absorption of water vapor at the silica gel in (g/24h-m²).

Biological protection tests

The penetration resistance of poliomyelitis virus in liquid was determined according to WSB58-2003. The temperature was 24°C, relative humidity was 65%. The penetration of poliomyelitis virus in liquid was determined at both atmospheric and negative pressures. Test procedures for determining biological resistance of garments for protection against the poliomyelitis virus in liquid:

B1 Test material

- B1.1 poliomyelitis virus suspended liquor, poliomyelitis virus TCID₅₀ $\leq 10^5$ TCID₅₀.
- B1.2 cell: cell which is compatible with poliomyelitis virus.
- B1.3 normal reagent of cultivating poliomyelitis virus.
- B1.4 vessel: plastic vessel with 25mm diameter, sterilize with pressurized steam.
- B1.5 sterilize filter apparatus .
- B1.6 dish utensil, sucker, containers and flask are all sterile.
- B1.7 vacuum pump
- B1.8 biology-resistant laboratory which is safe from a dangerous exposure to poliomyelitis virus.
- B1.9 fabric specimen: fabrics of biology-resistant garments for protection are cut into 50mm circles.

B2 Test method

B2.1 Sample preparation

Cut test specimens of biology-resistant garments and control fabrics and sterilize them with steam.

B2.2 Cultivate poliomyelitis virus

Operate by normal procedure.

B2.3 Test for poliomyelitis virus permeation under atmospheric pressure

Take two plastic vessels a 25mm diameter, put 3ml of liquor with suspended poliomyelitis virus (challenge liquid) into them, then cover the two vessels with a sample fabric and a control fabric, respectively and fix. Then invert them in the middle of sterile dish. Prick two holes with sterile forceps in the bottom of plastic vessels, and expose the containers to atmospheric pressure. At room temperature (20°C -25°C), the challenge liquid is free to permeates by gravity for 4 hours. Then one observes if the challenge liquid has penetrated the fabric. Any challenge liquid that has penetrated is taken up and subjected to the TCID₅₀. poliomyelitis virus test. If no challenge liquid has penetrated the fabric, wash the surface of sample fabric with 1-2ml cell keeping liquor, take washing liquor, and perform the TCID₅₀ test.

At the same time, perform the TCID₅₀ on the challenge liquid.

Repeat test three times.

B2.4 Test of poliomyelitis virus permeate under pressure

Under sterile conditions, take circular biology-resistant fabric for protection and control fabrics a circular diameter of 35mm and fix into sterile filtrate apparatus. Put 5ml poliomyelitis virus challenge liquid into filter apparatus, then cover the filter apparatus with a sterile closure to prevent contamination by air. Extract for 2 min under 0.5kPa/cm², Observe whether or not there is penetration of the challenge liquid. If there is some permeation of the poliomyelitis virus challenge liquid, take it up, and perform the TCID₅₀ poliomyelitis virus test. If there are no permeation of the challenge liquid, wash the surface of sample fabric keeping liquor 1-2ml of the cell liquor, take washing liquor, and do TCID₅₀ test. Observe effect of poliomyelitis virus permeation.

At the same time, test the TCID₅₀ of poliomyelitis virus challenge liquid .

Repeat test three times.

B3 Results evaluation

Resistant rate: If the average of three times test more than 99%, the specimens are up to grade. If less than 99%, the specimens are disqualified.

Airborne Challenge

The penetration resistance of animalcule (natural bacteria in the air) was measured according to WSB58-2003. The sample was cut into 50mm diameter circles. The temperature was 22-24°C, and relatively humidity was 55-70%. Test methods of Biology-resistant garments for protection against the animalcule in air as following.

A1 Test material

A1.1 laboratory of air animalcule

A1.2 catching animalcule and sampling system

A1.3 filter apparatus: 47mm diameter

A1.4 test animalcule: the nature animalcule in atmosphere

A1.5 washing liquor: 1% peptone with 0.5% TWEEN80.

A1.6 filter paper: 47mm diameter, aperture is 0.45µm.

A1.7 fabric specimen: fabrics of biology-resistant garment fabrics are cut in of 50mm diameter circles.

A2 Test step

A2.1 Sample preparation

Cut the sample into circles of 50mm diameter and steam sterilize.

A2.2 Sample fixed in filter apparatus

Test group, sample the specimen and put the filter paper into sterile filtrate apparatus under sterile conditions. Place specimen on the side of the entering air, before filter film .

Control group, put the filter film into sterile filter apparatus and sample the specimen under sterile conditions. Place filter paper on the air entering side before specimen. Put filter apparatus of two groups in the same sampling device, and send to the sampling place.

A2.3 Filtrate test

Connect the filter apparatus, test group and contrast group sampling at the same time. Note the flux, temperature and humidity simultaneously.

A2.4 Re-collection and note

Take down the filter film of the two groups, put them into washing liquor, re-collection animalcule and note data. Cultivate 48 hours under the condition of 37°C, then note amount.

A2.5 Count the number of re-collection animalcule colonies of two groups . Account resistant rate of specimen. Repeat test three times.

A3 Result evaluation

Resistant rate: If the average of three tests are more than 99%, the specimens are up to grade. If less than 99%, the specimens are disqualified.

Chemical protection measurement

(1)Liquid/liquid measurement

Mustard agent was used in the measurement. The mustard liquid was dropped onto the fabric, with a special testing paper on the rear as follows: Drip a fixed quantify toxin reagent on the specimen, put the specimen on the liquid test paper. Apply a force of 1.5g/cm² pressure to toxin reagent. After 360min, according to the level of color change determines the ability of the fabric to resist permeation of mustard agent under compression leading) The samples were considered to be eligible when the pressure is more than 1.47X10² Pa, and color of testing paper does not change.

(2)Liquid/gas measurement

5 micro-liter of mustard was dropped onto the fabric, with a special testing paper on the rear. According to the color change of the testing paper, we decided if the mustard agent passed through the fabric. If the color of testing paper did not change within 6 hours, the samples are considered to be eligible.

Procedure: Put the specimen on the indication paper on a ventilated cabinet, held at a temperature of 36°C. Drop 5µl of mustard on the specimen. After the specimen contacts the toxin reagent, toxin reagent begins to diffuse into the sample and onto the other side. Simultaneously the corresponding gas indication paper may show a color change indicating the end of the test. We call this time period "liquid-gas" toxin-resistant time that the materials resists the toxin reagent.

(3)Gas/gas measurement

The mustard gas was guided through a pipe to the surface of the fabric with a special testing paper on the rear. The temperature was 20±3?, relative humidity was 50%±32%. If the color of testing paper did not change within 6 hours, the samples were considered to be eligible.

Procedure for test method of GJB2394-1995: Get the toxin gas which contains a fixed quantify toxin (mustard gas) across the specimen. Use absorbing liquid (CH₃C(CH₃)₃OH,MIC) absorb the stream which penetrates through the specimen. Then use the DB-3 color antitheses test for the content of mus-

Table 1
PARTICULATE PENETRATION RESISTANCE OF PET FABRIC LAMINATED
WITH PTFE MEMBRANE

	Item		PET satin	PET twill
poliomyelitis virus in liquid	Atmosphere pressure	Starting	100%	—
		Washing 15 times	≥99%	—
	Negative pressure	Starting	100%	—
		Washing 15 times	≥99%	—
animalcule in air	Starting		≥99%	≥99%
	Washing 15 times		≥99%	≥99%

Samples	contact angle, °
PTFE membrane	120
Modified PTFE membrane	136

Table 2
THE CONTACT ANGLE BETWEEN THE PTFE
MEMBRANE AND WATER

tard gas in the absorbing liquid. Use this method to measure the toxin-resistant time that a quantity of mustard gas requires to be detected on the other side of the fabric, termed as “gas-gas” toxin-resistant time.

RESULTS and DISCUSSION

1. Penetration resistance of biological particulate

In this experiment, the penetration resistance of poliomyelitis virus in liquid and animalcule in air were measured. The results are shown in *Table 1*. It can be seen that the fabric provided excellent protection against biological particulate.

Table 3
EFFECT OF DIFFERENT THICKNESS OF PU ON PROTECTIVE
PROPERTIES OF PTFE/PU FILM

thickness of PU membrane on PTFE, μm	Liquid/liquid	Liquid/gas, min	Gas/gas, min
0, before modified	0	0	0
0, after modified	>1.47X10 ² Pa	22	7
10	>1.47X10 ² Pa	34	21
15	>1.47X10 ² Pa	73	53
19	>1.47X10 ² Pa	81	67
22	>1.47X10 ² Pa	101	89

2. Biological protective mechanism of the fabric

The size of bacteria and viruses is 10μm to 10-3μm. So it is difficult to separate these poliomyelitis viruses from air owing to the mean pore size of PTFE membrane (0.25μm). The PTFE/ PU complex membrane was developed in earlier studies (7, 8) to separate biological agents. The microporous structure of PTFE will prevent liquids such as perspiration containing poliomyelitis viruses from penetrating the film. However, bacteria and viruses suspended in aerosols or just in air can penetrate the ePTFE micropores. More complete protection is provided by putting a coating of a PU breathable monolithic (continuous film with no micropores) onto the PTFE. Since the PU film is impervious, the bacterial and viral particulate can not penetrate it. While blocking liquid perspiration, ePTFE will promote thermal comfort by allowing moisture vapor from perspiration to penetrate its structure and the PU component absorbs water chemically from perspiration in the liquid or gaseous state and allows it to evaporate through the other side of the membrane. Thus, biological agents can not permeate the PTFE/ PU complex membrane.

Furthermore due to low surface tension of PTFE membrane, liquid will not wet or adhere to the PTFE side in PTFE/PU membrane. Thus, the biological particulates in liquid can not penetrate through the membrane, and come into contact with the human skin.

3. Penetration resistance of mustard

Mustard liquid can wet through the PTFE membrane, so PTFE has scarcely any protective property. After the surface energy of PTFE membrane is further reduced by applying a fluorochemical (FC) finish as described above, mustard liquid can not permeate the membrane.

In order to discuss the mechanism, the contact angle between the PTFE membrane and water is measured. The results are shown in *Table 2*. From the data, it can be seen that the contact angle between water

Table 4
CHEMICAL PROTECTIVE PROPERTIES OF LAMINATED FABRIC TO MUSTARD AGENT

Item	thickness of PU membrane, μm	Liquid/liquid	Liquid/gas	Gas/gas
1	10	$>1.47 \times 10^2 \text{Pa}$	$>6\text{h}$	$>6\text{h}$
2	15	$>1.47 \times 10^2 \text{Pa}$	$>6\text{h}$	$>6\text{h}$
3	19	$>1.47 \times 10^2 \text{Pa}$	$>6\text{h}$	$>6\text{h}$
4	22	$>1.47 \times 10^2 \text{Pa}$	$>6\text{h}$	$>6\text{h}$

Table 5
EFFECT OF THICKNESS OF PU MEMBRANE COATED ON WVP ($\text{G}/24\text{H}\cdot\text{M}^2$)

Item	thickness of PU membrane, μm	WVP of PU membrane	WVP of PTFE/ PU membrane	WVP of laminated fabric*
1	10	17290	16532	6790
2	15	16587	14312	6201
3	19	15421	12780	4789
4	22	13496	12341	4452

*: The fabric against CB warfare agents

and the PTFE film is increased due to the FC treatment. This indicates the reduced surface energy of the PTFE membrane will cause the mustard to slide from the protective laminated fabric, thereby preventing the mustard agent from permeating the membrane.

The PU coating will form a film during coating and drying. Not only is the PU film important to separate the biological warfare agents, but also has an effect on the chemical liquid and biological warfare agents. From the data in Table 3, it can be seen the protective properties increase with an increase in thickness of PU film.

From Table 3, it can be also seen that the modified PTFE membrane can prevent the mustard liquid from permeating, but gas still can penetrate the membrane. Any residual mustard gas can be absorbed by active carbon felt. It can be seen that the laminated fabric with activated carbon fiber felt has good protective properties against CB warfare agents from Table 4.

Additional work is underway to determine if a felt of needle-punched activated carbon fibers can absorb residual mustard agent gas as well as the more proven activated carbon granules.

4 WVP

As shown in Table 5, the WVP of PU membrane is decreased with increasing thickness of the PU membrane, which also reduces WVP through the laminated structure. Water vapor molecules selectively dissolves into the PU coating, diffuses across the PTFE membrane, and desorbs into the environment, while organic vapor molecules are not absorbed by the hydrophilic PU and are thereby prevented from per-

meating through its polymeric material structure.

As a protective material, the laminated fabric can significantly reduce heat stress and the physiological heat load to the wear, thereby providing satisfactory wearing comfort.

Conclusions

The CB protective material was prepared in the following manner: the PET fabric was laminated with modified PTFE membrane by paste dot coating, and then coated by PU solution in a direct process. Finally, it was laminated with an active carbon felt.

The CB protective material can prevent mustard liquid and biological warfare agents from permeating through the laminate. Any residual mustard gas penetrating the PU film should be absorbed by active carbon felt, which will be the subject of further study. The high MVP of the laminated fabrics should also enhance wearing comfort.

Acknowledgements:

Financial support of this project from the Beijing Natural Science Foundation of China with the Program grant number of 2052016 is thankfully acknowledged.

We are very grateful to Prof. Larry C. Wadsworth of the Materials Science & Engineering Department, University of Tennessee for helpful critical suggestions.

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