Employment of Simulants for Testing Constructive Materials Designed for Body Surface Isolative Protection in Relation to Chemical Warfare Agents

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Employment of simulants, thus spare testing compounds always takes the bigger value in the area of testing garments designated for body surface protection against the effects of chemical warfare agents. The aim of simulants usage is mainly to remove problems related to manipulation with high toxic compounds and to enable testing to such working places that have not got the permission for the treatment with chemical warfare agents and other highly toxic compounds. The paper summarizes some achieved results of measurements of chemical resistance which have been performed based on simulants. These results are put into mutual connection with the sulfur mustard which is recently used as a standard testing chemical compound.

Key words: sulfur mustard, bis(2-chloroethyl) sulfide, methyl salicylate, 1,6-dichlorohexane, simulant, Piezotest

Generally, a technological process of making a product (with all its stages, from the idea to the resulting waste) aims to achieve satisfactory economic performance for the producer and a quality product for the beneficiary (in this case the military). Thus, information from numerous research fields correlate to ensure maximum productivity and getting optimum finite products [1-12]. The permanent qualitative evaluation of materials produced for the use of the army and the innovation of new ones, with better protection performances, require an efficient and sustainable management from industrial producers in the field [5,6,13-20].

All activities that take place during the production process of military uniforms or equipment of protection are under strict observation and continuous assessment. An important issue is to solve the problem of protection against chemical warfare agents (CWAs).

Sometimes, a lot of these substances (pharmaceuticals which under normal conditions and specified doses are beneficial to health) can often be found in the environment as wastes / pollutants, affecting in this case the life and health of living organisms depending on the concentrations in which they are found [21-29]. Moreover they are harmful when they are intentionally used in overdose, toxic doses or in lethal doses during wartime.

Employment of simulants, thus spare testing compounds always takes the bigger value in the area of testing garments designated for body surface protection against the effects of chemical warfare agents. The aim of simulants usage is mainly to remove problems related to manipulation with high toxic compounds and to enable testing to such working places that have not got the permission for the treatment with chemical warfare agents and other highly toxic compounds. Although the employment of simulants for testing constructive materials of personnel protective equipment seems to be advantageous at first sight the results of experiments with simulants do not have to response to testing with the real chemical warfare agent (CWA).

The CWA like bis(2-chloroethyl) sulfide (known as sulfur mustard) is a prototypical substance of the sulfur-based family, being a cytotoxic and vesicant CWA which form large blisters on the exposed skin and in the lungs. It is traditionally used for testing constructive materials of personnel protective equipment. This agent has a relatively simple chemical structure (fig. 1).

Fig. 1. Chemical structure of sulfur mustard

From the group of persistent compounds it is less toxic than the others, it is relatively available, it has a small molar volume in comparison with others persistent CWA, and it is easily detectable with simple detection devices which can be used for detection of permeated test chemical through constructive materials. The testing is performed at the temperature of 30 °C.

Choosing of a particular simulant depends on the purpose of it usage. As simulants of the sulfur mustard it is used a great number of compounds with very different chemical structure (table 1), implicitly diverse physical and chemical properties, and moreover, different toxicity.

The 1,6-dichlorohexane and methyl salicylate are named as the simulants concerning the sulfur mustard for determination of chemical resistance of personnel protective equipment constructive materials. In accordance to Lavoie's information (who for the proposal of suitable simulant of the sulfur mustard has used a software working with chemo metric tools) and with the help of Tanimot's coefficient of similarity and Euclid's distance between the chemical substance and the simulant, it has been demonstrated that the ideal simulant is the compound with the similar chemical structure.

In the case of the sulfur mustard is as the most suitable simulant for both tested values named 2-chloroethyl ethyl sulfide and subsequently 2-chloroethyl methyl sulfide. On the other hand, methyl salicylate has been assessed as the less suitable in both cases.

A method of selecting compounds that can mimic the pharmacological activity of both synthetic and natural medical products has thus developed. This also results from a combination of physicochemical properties

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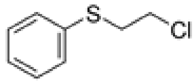
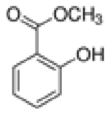
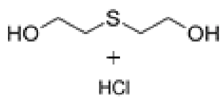
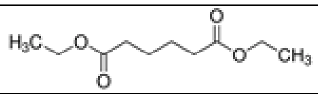
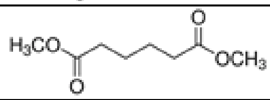
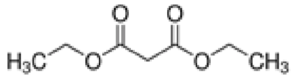
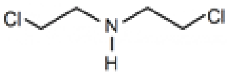
Substance	Chemical Formula	Substance	Chemical Formula
2-chloroethyl ethyl sulfide [30-32]		bis(2-chloroethyl) ether [33,34]	
1,6-dichlorohexane [30,35]		bis(4-chlorobutyl)ether [33]	
n-octane [33]		(2-chloroethyl)fenyl-sulfide [32,34,36,37]	
1,5-dichloropentane [38]		dibutylsulfide [39,40]	
ethyl 2-hydroxyethyl sulfide [39]		ethylene glycol [33]	
methyl salicylate [32,41]		2-chloroethylfenyl sulfide [43]	
mixture of thiodiglycol and hydrochloric acid [42]		diethyl pimelate [32]	
diethyl adipate [32]		2-chloroethyl ethyl ether	
dimethyl adipate [32]		bis(2-bromoethyl) sulfide [43]	
diethyl malonate [32]		2-chloroethyl methyl sulfide [43]	
bis(2-chloroethyl) amine [43]		thiodiglycol [43]	

Table 1
CHEMICAL STRUCTURE OF THE SIMULANTS

(molecular weight, refractive index, solubility, dipole moment, melting point, boiling point, saturated vapor pressure, dissociation constant, spectral characteristics, etc.) of the simulants substances. Conclusions can therefore be applied even to substances used for the testing of construction materials for the protection of body surfaces and organs respiration.

Experimental part

Apparatus

The devices used in the experimental part were as follows: Biological thermo-regulator Friocell 111 (Brnenska medicinska technika Brno, Czech Republic), quick thickness meter Mitutoyo, typ 542-401 (Mitutoyo Corporation, Japan), Piezotest, equipment for breakthrough times measurement (Gryf HB, Limited Company, Havlickuv Brod, Czech Republic), hydraulic press (Polymertest, Limited Company, Zlin, Czech Republic), cutter of samples (Marbach, limited company, Brno, Czech Republic).

Reagents

Reagents used were: Bis(2-chloroethyl)sulfide – sulfur mustard (VOZ 072, Zemianske Kosto¾any, Slovakia, amount of the effect compound 96.7 %), 2-chloroethyl ethyl sulfide, 98 % (Sigma-Aldrich, Germany), methyl salicylate, ReagentPlus(Sigma-Aldrich, Germany), 1,6-dichloro-hexane, for synthesis (Merck-Schuchard, Germany).

Tested materials

Materials tested were: isolative protective textile of TP-RUB-001-06, polyamide textile both-sided coated with butyl-rubber (Rubena, Public Limited Corporation, Hradec Kralove, Czech Republic) and the self-contained foil made of polyethylene-vinyl acetate (Fatra, Public Limited Corporation, Napajedla, Czech Republic).

Working procedures

Test samples have been cut from the isolative protective foils with the help of the cutter of samples and the hydraulic press. Using the quick thickness meter the thickness of test samples have been measured in millimeters with the accuracy of three decimal positions. From test samples four sets have been made. Each set contained approximately same representation of samples with explicit thickness measured in the middle part. The sets have been formed in order to have approximately the same thickness of samples. Samples have been fixed into a test part of the Piezotest device permeation cells, both parts, thus the test part and measuring parts have been completed and after that put into the biological thermo regulator within 30 min to reach the temperature of 30 °C.

2 mL of each tested chemical has been dosed into each permeation cell. At this time the special software has been launched. The device has been stopped after necessary time of measurement which has been specified with drawing of a linear part of dependence of the change (addition) of working frequency on time has been achieved. From the graphical dependence of the permeation curve the breakthrough time has been deducted.

Results discussions

The tested isolative protective foil has been relatively homogenous from the point of their thickness point of view as evidenced by the middle value of the thickness (fig. 2).

Minimal thickness for sets of samples has differed only minimally. It has enabled to perform mutual comparison of the breakthrough time of isolative protective textile for selected test chemicals.

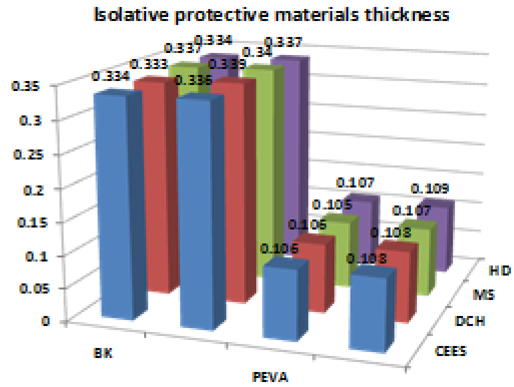


Fig. 2. Thickness of the set of samples of isolative protective materials for tested chemicals (CEES - 2-chloroethyl ethyl sulfide; DCH - 1,6-dichlorohexane, MS-Methyl salicylate; HD -sulfur mustard; BK-textile both-sided coated with butyl-rubber; PEVA - foil made of polyethylene vinyl acetate; the first values at BK (PEVA) - minimal values of thickness; the second values at BK (PEVA)- mean values of thickness)

Results of measurements of constructive protective materials breakthrough time for tested chemicals are introduced in figure 3.

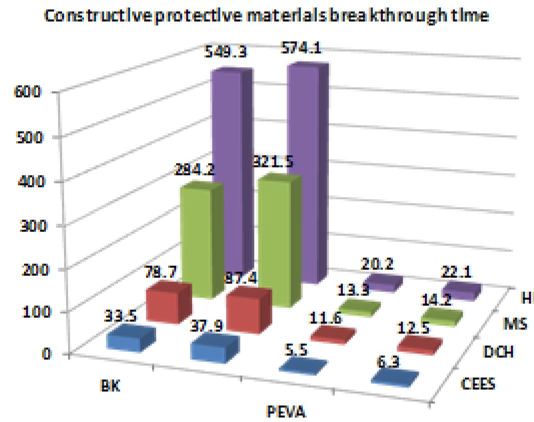


Fig. 3. Results of measurements of constructive protective materials breakthrough time for simple tested chemicals (CEES -2-chloroethyl ethyl sulfide; DCH- 1,6-dichlorohexane, MS-Methyl salicylate; HD-sulfur mustard; BK- textile both-sided coated with butyl-rubber; PEVA-foil made of polyethylene vinyl acetate; the first values at BK (PEVA)-minimal values of Breakthrough time; the second values at BK (PEVA)- mean values of Breakthrough time)

As it is evident from results of the measurements both isolative protective foils have had the biggest resistance for the sulfur mustard.

The mean value of the breakthrough time was 574 minutes and minimal value of breakthrough time which has bigger value for evaluation from the real protective properties point of view was 549 min for this chemical. For PEVA foil the middle value of the breakthrough time was 22 min and minimal value 20 min. Within this foil the resistance against the sulfur mustard was significantly lower regardless of the fact that its thickness was only one third in comparison with the textile with a butyl-rubber barrier layer.

It is noticeable that butyl-rubber belongs to the group of non-polar polymers and it has high chemical resistance for the sulfur mustard. In relation to the sulfur mustards it was not possible to find values of relative permittivity which indicate the chemical compound´s polarity. If we, however, get out from the chemical structure it is the simple bis(2-chloroethyl)thioether. An oxygen analog of the sulfur mustard it is bis(2-chloroethyl)ether. This chemical compound has the relative permittivity equaled 21.20 (20 °C) and from this reason it is strongly polar substance. Within this chemical a covalent polar bonds there are between the carbon and chlorine atoms (electro negativity difference is ΔX_{C-Cl}=0.61) and between the carbon and oxygen atoms (ΔX_{C-O}=0.89). This probably causes the high polarity of this compound.

Although it is not possible to deduce a simple analogy between relative permittivity of both compounds because the bond carbon-sulfur has the character of covalent non-polar bond (ΔX_{C-S}=0.03) and the overall polarity of the sulfur mustard probably significantly does not influence the presence of ethyl alkyl with the covalent polar bonds between the carbon and chlorine atoms by both compounds probably significantly influences their polarity. High values of chemical resistance of isolative protective folio with the butyl-rubber barrier layer response to this presumption for this compound as well.

Different situation is in the case of 1,6-dichlorohexane. This chemical compound has a pair of bonds between the chlorine and carbon atoms and these bonds have the character of the covalent polar bond (ΔX_{C-Cl}=0.61). Although we can speak about non-polar chemical substance in accordance to the value of relative permittivity (table 2) its non-polar character is not so expressive as, for example it the case of benzene (ε_r=2.2825; 20 °C) or tetra chloromethane (ε_r =2.2379; 20 °C) for those the butyl-rubber has very small chemical resistance, ordinal only few minutes.

Even the value of the breakthrough time which has the mean value of 87.4 min and minimal value almost of 79 min responses to the non-polar character. The same conclusion has been possible to make even within the foil made of polyethylene-vinyl acetate whose mean value of the breakthrough time was 12.5 min and minimal value of breakthrough time 11.6 min. It is thus evident that 1,6-dichlorohexane has absolutely different properties than sulfur mustard from the permeation point of view.

Both constructive materials embodies higher value of resistance for methyl salicylate in comparison with 1,6-dichlorohexane. Middle value of the breakthrough time for

Table 2
SELECTED PHYSICAL VALUES OF CHEMICALS TESTED

Chemicals	Molecular weight M_r [g/mol]	Melting temp. t_t [°C]	Boiling temp. t_v [°C]	Density ρ [g/cm^3]	Molar volume V_m [cm/mol]	Relative permittivity ε_r (°C)
Bis(2-chloroethyl) sulfide	159.07	14	228	1.27	125.251	-
2-chloroethyl ethyl sulfide	124.63	-48.66	154.73	1.07	116.477	-
1,6-dichlorohexane	155.07	-13	116-117	1.07	144.925	8.60 (35 °C)
Methyl salicylate	152.149	-8	220-224	1.184	128.504	8.80 (41.3 °C)

this compound was 321.5 min and the minimal value 284.2 min.

In the case of foil made of polyethylene vinyl acetate thus these values did 14.2 and 13.3 min. It is visible that two compounds with very similar value of relative permittivity show very different values of permeation through test material.

If we take into account the molar volumes of both compounds (Table 2), with this parameter is not possible to explain a different ability of permeation of these substances because the compound with lower value of the molar volume permeates longer time which does not response to general presumptions of toxic compounds permeation through polymeric materials.

From the survey table of physical data (table 2) it is clear than methyl salicylate advances towards to the sulfur mustard. Different polarity of both compounds eventuality affects the rate of permeation of both compounds through tested material. It is thus evident that similarity of physical properties cannot be the main criterion of the choice the chemical compound as the stimulant for determination of chemicals resistance of the protective garments constructive materials.

From the chemical similarity point of view the most similar simulant is 2-chloroethyl ethyl sulfide in comparison with the sulfur mustard. This compound, however, has permeated through both constructive materials in the quickest way. It has not been possible to found the value of relative permittivity in available literature. The bond between the carbon and the chlorine has the character of polar bond (X_{C-Cl}=0.61).

On the other hand, the bond between carbon and the sulfur has the character of the non-polar bond. In terms of the rate of permeation this chemical compound should have the non-polar character. Named chemical has the smallest molar volume from all test chemicals. This fact would be generally important for permeation of 2-chloroethyl ethyl sulfide. In the case of non-polar character of the compound the permeation through non-polar polymers can be significantly influenced. Without reference to these presumptions the similarity of the chemical structure of the sulfur mustard and 2-chloroethyl ethyl sulfide does not prove the advantage of 2-chloroethyl ethyl sulfide employment as the simulant of the sulfur mustard.

Conclusions

Measurements of chemical resistance have shown that mainly for high toxic chemical compounds of the type of CWA (chemical warfare agents) it is necessary to perform practical measurements of the resistance of constructive materials and not for their simulants.

Furthermore, practical measurements have shown that simulants of the sulfur mustard recommended in professional literature are not able to replace particular chemical compounds. Even the work with simulants can be advantageous for their chemical and toxicological properties it is necessary to observe the particular aim of the employment of the concrete chemical compound.

It is understandable that for their toxicity the usage of mainly CWA for testing of constructive materials is very problematic.

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