Characterization of a New Bromobutyl Rubber Composite for NBC Protection

I. Protection properties

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Since discovered, rubbers were tested, among other possible utilizations, for their military use. In the present study, NBC protection properties of a new bromobutyl rubber-based composite (BrBR) are presented: protection time against liquid droplets of mustard gas (also known as yperite, 1,5-dichloro-3-thiapentane or HD), flame resistance and flame propagation properties.

The tests performed demonstrated the improvement brought by BrBR in comparison with the materials in use in the Romanian army, this material offering the same protection level as the materials used nowadays in developed countries.

Keywords: NBC protection, composites, mustard gas, burning time

The probability of using nuclear, biological or chemical (NBC) warfare agents leads to the necessity of adopting protective measures, in order to avoid both military and civilian contamination and to reduce the casualties. Another reason for the need of protective measures is due to the risks of accidents, terrorist actions, sabotage or cataclysms involving chemical or nuclear plants [1-7].

The materials best suited for NBC individual protection equipment (NBCIPE) manufacturing are included in two main categories [8-10]:

-thermoplastic polymers, such as polyesters, polyamides, polyformaldehydes, polysulphones and polycarbonates. Both threads and foils present satisfactory properties for using in NBCIPE manufacturing. Because of their rigidity, they need plasticizers addition in order to increase the flexibility, thus increasing to an unacceptable level the permeation of chemical warfare agents (CWA);

-elastomers, where two major aspects are considered when researching the protection characteristics of foils against liquid CWA: direct sorption in material structure and permeation through material.

Natural rubber (NR) was the first elastomer tested for permeation to mustard gas (also known as yperite, 1,5-dichloro-3-thiapentane or HD), which gives a permeation time of 50 min. All other known elastomers present similar permeation (or protection) values (between 50 min and 2 h), excepting three of them [11-16]:

- silicon rubber, with a very low protection time (less than 5 min);

- perfluorocarbonates (such as Viton and Fluorel) present protection time of approximately 7 days. These are the most performant elastomers, but they are not used in NBC protection because are costly, need toxic additives in the processing stage (thus being relatively toxic to the skin) and cannot be used at low temperatures because of dramatical decrease of their elastic properties;

- butyl rubber and also butyl rubber-based mixtures present protection time of about 2 days, no matter the copolymer used or whether the butyl rubber is halogenated or not. Butyl rubber is relatively cheap, can be processed with nontoxic additives and its mechanical properties make it a good choice for NBCIPE manufacturing. Halobutyl rubbers are less influenced by low temperatures and their protection times against HD droplets are 60 times better than natural rubber (table 1).

No.	Material	Protection time against HD (minutes)
1	Plasticized polyvinylchloride	< 20
2	Silicon rubber	< 4
3	Styrene butadiene rubber	< 20
4	Neoprene rubber	< 30
5	Polyethylene	< 10
6	Butyl rubber	> 480
7	Nitrile rubber	~ 120
8	VITON or FLUOREL	> 10.000

Table 1
PROTECTION TIME OF DIFFERENT MATERIALS [11-16]

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Table 2
BRBR COMPOSITION

No.	Material	%
1.	Brombutyl rubber	39 – 42
2.	Butyl rubber	9 – 12
3.	Polyethylene	4.5 – 7
4.	Magnesium oxide	0.3 – 0.6
5.	Chromium oxide	9.5 – 11.7
6.	Stearine	0.5 – 0.7
7.	Chlorinated paraffin	7.8 – 8.5
8.	Zinc oleate	0.9 – 1.3
9.	Silica oxide	11 – 12.5
10.	Vulcacit	0.01 – 0.1
11.	Antioxidant	0.2 – 0.6
12.	Antimony trioxide	7.8 – 8.5
13.	Sulphur	1.5 – 2.5

NBC protection properties of a new bromobutyl rubber-based composite (BrBR) are presented in this study. The characterization of this composite was based on the comparison of its properties with those of similar NBC protection materials, used either in Romanian Army or in other NATO country armies.

Materials and methods

BrBR is a bromobutyl/butyl rubber mixture, in a ratio of 4/1, with the composition presented in table 2.

The materials used to test comparatively the new NBC protection material submitted to evaluation (BrBR) were: Opanol material (OP), consisting in a composite of NR on cotton; BP/SP (Butyl rubber on Pandora polyester); BC/SP2 (Butyl rubber on a second generation Pandora polyester); M1 material (a German multilayer butyl rubber); M2 material (a French composite of bromobutyl rubber on polyester).

There are not provided in the literature composition data for the OP, M1 and M2 materials. The other three materials tested had the elastomer composition illustrated in table 3 and contained the following compounds: reinforcing agent (silicon dioxide), vulcanizing agents (sulfur, zinc oxide, and barium stearate), flame retardant agents (paraffin chloride and antimony trioxide), and chromium oxide as green pigment (table 2).

Morphology and homogeneity determinations for the new material, BrBR, were performed through Scanning Electron Microscopy (SEM) using a Philips XL30 - ESEM Turbo Molecular Pump (TMP), at 25 keV.

In order to evaluate the protection properties of the BrBR, the material was characterized according to the end user requirements. For the validation of the obtained results, comparative tests were performed, either with materials used for the manufacturing of the NBCIPE existent in the Romanian army (Opanol material, BP material, BC/SP2 material), or with materials used abroad for NBCIPE manufacturing (M1- German material, M2 – French material).

The tests were performed using the same apparatus, under the same conditions, and using the same standardized methods (where possible) or methods validated within the Laboratory of NBC Protection Equipment from the NBC Defense and Ecology Scientific Research Center, in order to avoid any difference resulted from the method or testing equipment used.

The most important parameter for insulating NBCIPE is the protection time against liquid CWA. There were also performed flame resistant tests, in order to evaluate the possibilities of using the material in operational conditions.

<u>Determination of protection time against liquid droplets of CWA</u>

The method used for the determination of protection time against liquid droplets of CWA consisted in statically

Table 3
ELASTOMER COMPOSITION FOR THREE OF THE MATERIALS USED

Material / Elastomer composition	BrBR	BP/SP	BC/SP2
Chloroprene	-	-	9-12
Butadiene rubber	-	-	0.8-1
Chlorobutyl rubber	-	-	50-55
Butyl rubber	12-22	65-71	18-20
Polyethylene	8-13	29-35	10-15
Bromobutyl rubber	70-75	-	-

test against HD droplets, at a contamination density of 10g/m^2. The tests were performed in an oven, at 36.5°C.

HD diffuses through the materials, until it penetrates the entire material and exits on the side opposite to the contaminated one. At the contact with an indicator textile layer impregnated with a chloramine and Congo red as pH indicator, HD reacts with the chloramine, resulting hydrogen chloride, which turns the color from red to blue.

Samples were drawn from the protection materials and from the indicator layer. The sampling was performed from different parts of the material, representative for the material condition.

The samples were put into an apparatus, in the following order: the material sample, a gauze round, the indicator layer (fig. 1). Further, the samples were conditioned at 36.5°C for 30 min, and afterwards they were contaminated with HD droplets.

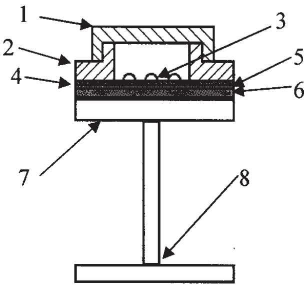

Fig. 1. Apparatus for liquid chemical agents testing. 1 - lid, 2 - superior part, 3 - HD droplets, 4 - material sample, 5 - gauze round, 6 - indicator layer, 7 - glass round, 8 - inferior part

Determination of flame resistance

A James H. Heal burning chamber, Flexiburn 780, with the following characteristics: gas: propane; gas pressure: 5÷10 psi; test temperature 10÷30°C; flame length: 10 mm ÷ 60 mm, was used for the tests.

Determination of burning behavior of horizontally oriented samples

Samples were conditioned at (20 ± 2) °C and relative humidity of (65 ± 5) % for minimum 24 h. The testing conditions conserved the following parameters: 10 to 30°C temperature, 15 to 80% relative humidity and 0.2 m/s wind speed.

The distance to flame was set to (25 ± 2) mm, in agreement with [17]. A testing flame was applied for 10 s and it was observed whether the material burns or not, and, in the first case, the self-extinction time.

Determination of flame propagation properties on vertically oriented samples

Samples were conditioned in the same manner as presented previously. The flame was applied for 10, 15 and 20 s. The following data are recorded, in agreement with [18]:

- time, in seconds, from the start of the flame application until the destruction of the marking thread from the bottom (the first one);
- time, in seconds, from the start of the flame application until the destruction of the marking thread from the middle (the second one);
- time, in seconds, from the start of the flame application until the destruction of the marking thread from the top (the third one).

Results and discussions

SEM analysis

Since the homogeneity of the material represents a very important parameter, considering the application field, the first step of this study consisted in SEM morphological investigation of the obtained rubber. The images from figure 2 show that BrBR synthesized was obtained as a homogenous material. Therefore, the material is morphologically appropriate to be further used as protective material.

Protection time against HD droplets

The comparative results obtained during the determination of protection time against HD droplets with 10g/m^2 contamination density are given in figure 3.

The tests carried out demonstrated the improvement brought by BrBR (> 1440 min) in comparison with the materials in use in the Romanian army (72, 134, and 157 min, respectively), this material offering the same protection level as the materials used nowadays in developed countries. The low percentage of polyethylene in the new BrBR material, compared with the other two Romanian materials, is the main reason for this improvement.

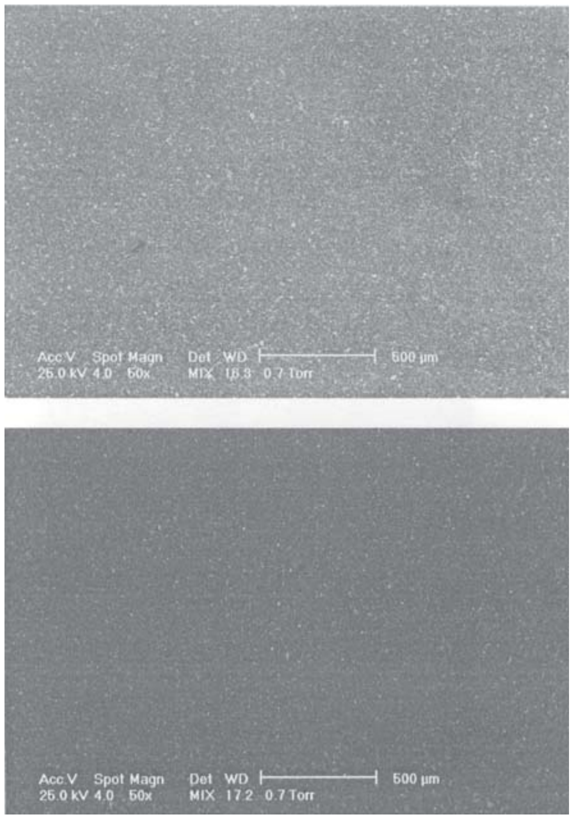

Fig. 2. SEM microphotographs of BrBR material

Self extinction time

This parameter was determined through a propane flame application for 10 s on vertically samples and self extinction time was measured.

The results of the tests performed are presented in table 4.

The conclusions drawn from the experiment consist in a clear difference among new generation materials (M1, M2 and BrBR), which did not burn after a 10 s flame application, and the old generation materials.

Even though the old generation materials burnt, they maintained their capacity of self-extinction, but during different periods of time. A rather newer material (BC/SP2 - 25 s) is not necessarily better than an older one (BP

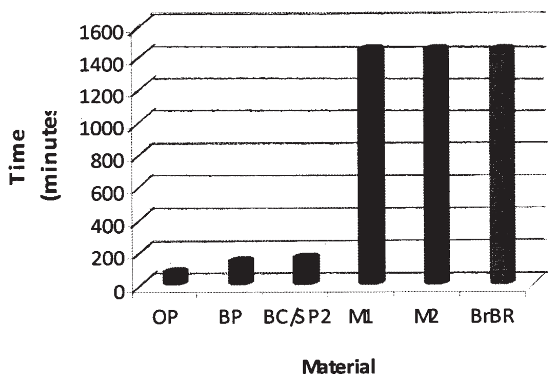

Fig. 3. Protection time against HD droplets (the tests were stopped after 24 h, the maximum protection time required by the end user)

Table 4
SELF EXTINCTION TIME

Material	OP	BP	BC/SP2	M1	M2	BrBR
Self extinction after 10 seconds, seconds	n/a*	14	25	n/a**	n/a**	n/a**

* = The material did not extinct by itself; ** = The material did not burn after flame application.

Table 5
FLAME PROPAGATION TIME

Determination	Distance	OP	BP	BC/SP2	M1	M2	BrBR
10 second flame application							
Flame propagation time, seconds	220 mm	47.7	8.2	20.1	n/a**	n/a**	n/a**
	370 mm	57.2	11.7	22.3			
	520 mm	58.7	13.5	n/a*			
15 second flame application							
Flame propagation time, seconds	220 mm	37.7	7.9	17.5	n/a**	n/a**	n/a**
	370 mm	45.2	10.2	19.7			
	520 mm	48.8	11.5	21.5			
20 second flame application							
Flame propagation time, seconds	220 mm	15.2	5.8	14.6	45.8	37.4	22.4
	370 mm	18.3	6.2	18.8	138.2	120.1	112.4
	520 mm	20.1	7.4	20.0	149.7	124.9	115.8

*=The material did extinct by itself after 25 seconds; ** = Did not burn;

-14 s), but BC/SP2 presents better mechanical and resistant characteristics against CWA. The only material without self-extinction properties is the one containing natural rubber.

Flame propagation

In order to identify the propagation rate of the flame on the material, identification bench-marks were set at 220, 370 and 520 mm from the flame application point.

Taking into consideration that, after a 10 s -application of the flame, some materials did not burn, the flame propagation tests consisted in up to 20 s flame application, in order to be able to hierarchise the materials after their burning behaviour.

The results obtained are given in table 5.

According to the data in the table 5, the propagation time (for each mark) decreased for each material as the flame application time increased. Also, for every particular material, propagation time for the three marks (220, 370 and 520mm, respectively) decreased as the flame application time increased.

M1 and M2 materials presented better propagation time than BrBR, meaning that the time to reach every mark were higher for M1 and M2 than for BrBR.

BrBR proved to have excellent flame protection properties, fulfilling entirely the requirements of the end user (did not burn after 10 s flame application) and, in addition, after 20 s flame application, self extinction time is less than 2 min.

Conclusions

During war, one of the first concerns is to protect military and civilians against a possible chemical attack. Therefore, continuous research is performed in order to improve the parameters of the protection equipment. In the present study, protection properties of a new bromobutyl-based composite were evaluated versus other materials in use, obtaining very good results.

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Manuscript received: 24.06.2010