Polyurea-based Hybrid Composites for CBRN Protection

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Either considering chemical munitions or chemical improvised explosive devices, the armies should be able to counter their effects from two different perspectives: the agent used and the way to disperse it. While the agent to be delivered can be more or less lethal, the real factor that gives efficiency to the attack is the manner the agent is delivered. The state-of-the-art tested garment indicate that current knowledge regarding protective equipment for chemical warfare agents remains very limited. In this context, the present study aimed at the possibility of using the MWCNT-OH-based polyurea-composite material, obtained by our group in a previous study, in the field of protection against hazardous chemicals.

Keywords: chemical warfare agent; protection equipment; decontamination

Chemical Weapons (CWs) represent a perpetual state-of-the-art threat the international community has to cope with. Since the First World War through the Second World War to events in Syria, there had been cases where various types of Weapons of Mass Destruction (WMDs) have been used.

The new challenge regarding CWs is the change of their use. If, in the past, chemical agents were or could only be used by Nations, currently the threat may come from non-state actors or violent extremist organizations using this type of unconventional weapon, rendering it as an efficient weapon capable to provoke a high amount of casualties [1-3].

The panoply of warfare chemical toxics has expanded to include choke, blister, asphyxiation or paralyzing agents. Although similarities of these chemicals with toxic industrial chemicals (chlorine, phosgene, hydrogen cyanide, etc.) exist, knowledge on their effects is limited [4]. Historically, one of the most dangerous, used and important tactical agents is sulphur mustard (HD or yperite), which is a vesicant alkylating agent that incapacitates the enemy. The weapon of choice in modern tactical warfare, HD, due to its low volatility, vaporizes slowly, implying a particular risk in prolonged, closed-space or below-grade exposures. At higher temperatures, vaporization increases and contributes to more severe clinical effects. At temperate climates, in open areas with little or no wind, it has been proved that it persists for one week. Persistence at temperatures over 37.7 ºC is of one day. On the contrary, sarin (GB) is the most volatile of the nerve agents, presenting almost an immediate life threat.

Either considering chemical munitions or chemical improvised explosive devices, the armies should be able to counter their effects from two different perspectives: the agent used and the way to disperse it. While the agent to be delivered can be more or less lethal, the real factor that gives efficiency to the attack is the manner the agent is delivered. Thus, especially during combat operations and taking into account these concerns, it is of tremendous importance for the soldiers to be protected against mechanical and physical aggressions, including against any type of potentially harmful environment. In this regard, the individual and collective protection equipment (PE) has to prove high resistance against various toxic industrial hazards and/or chemical agents.

The state-of-the-art tested garment indicate that current knowledge regarding PE for chemical warfare agents (CWAs) remains very limited [5].

While countering a chemical, biological, radiological, and nuclear (CBRN) attack, the availability and quality of protective clothing is of tremendous importance, in order that the operators feel both safe and comfortable during missions. The combat staff, either acting in urban areas or theatres of operation, must be kept safe against this kind of threats, meanwhile maintaining a bearable weight of the equipment. Furthermore, it is necessary to prepare the civil population against a possible CBRN attack not only by developing new defence products / PE, but also by making the existing technologies widely available from economically point of view.

Protection clothing for military and police forces must offer CBRN protection, meanwhile being designed so that they can be used for days without doffing, must be easy to clean and maintain, have relatively good drape and comfort, and must still be relatively low in weight, particularly where the user may have other heavy equipment to carry [7-10]. The degree of physiological burden depends on individual parameters of the skin, body and environment temperature and pressure, moisture and the movement of the air inside the protective clothing. In this view, one of the most important parameters when considering PE, is the air permeation. Non-porous breathable membranes of, e.g.,

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polyesters, polyether amides or polyurethanes between two layers of textile that permits the passage of water vapour, but do not let the toxic chemical penetrate, allow that water vapour pass to the exterior making the clothes more comfortable and helping to maintain the physiological stability [5,11].

An important number of papers studied the possibility of developing more protective garment, while maintaining an equilibrium between protection and comfort [5-9]. Dupont's Tyvek®, a flashspun polyethylene nonwoven, and Kimberly-Clark's Kleenguard®, a spunbond-meltblown-spunbond (SMS) polypropylene fabric, are been extensively used for their liquid- and vapor repellent features and hydrophobicity [7].

The present study considered the available data from literature, but also aimed at the possibility of using the novel polyurea-based composite material obtained by our group for ballistic PE [12] also in hazardous chemicals protection.

Experimental part

Materials and methods

Materials

The same materials and the same fabrication conditions were employed as in [12]. In brief, polyurea (PU) and four MWCNT-OH-polyurea derivatives (PUCs) have been obtained from respective components (Table 1), starting from a 10% MWCNT-OH masterbatch. The polymer obtained has been applied by direct continuous-layer spraying through a pressurized container at 150 bar and 65 ° on various layers, in different thicknesses: 0.55, 1.20, 1.75 and 2.30 mm.

Three types of gloves have been used as support layer: nylon-cotton safety gloves (Glove1) and cotton safety gloves (Glove2) from DALGECO®, and cotton safety gloves from DRÄGER®.

Table 1
RATIOS OF THE COMPONENTS IN THE POLYMER AND IN THE COMPOSITES [12]

Composite material	**Polyurea prepolymer (wt%), EUROPOL®**	**Polyamines (wt%), EUROPOL®**	**MWCNT–OH Reinforcing agent (wt%)**
PU	50	50	-
PUC1	49.40	49.40	1.20
PUC2	49.50	49.50	1.00
PUC3	49.625	49.625	0.75
PUC4	49.70	49.70	0.60

In figure 1 are illustrated the steps pursued for the support materials (chemical protection materials) obtainment, by simple operations and equipment.

a  b

Fig. 1. a) Pulverization of PUC on support layers;
b) Protection gloves before and after treatment

Thermogravimetric analysis

Thermogravimetric curves have been recorded on a Q500TA instrument, under nitrogen atmosphere, at a 10 °C/min. heating rate from room temperature to 600 °C.

Scanning electron microscopy

SEM and EDX have been carried out on a VEGA II LMU equipment, at a 3.5 nm resolution and 30 keV, and an EDX analyzer Bruker AXS Microanalysis AG, Germany.

Protection evaluation against CWAs

The PUCs have been tested against CWAs and the protection time has been determined, in agreement with [13]. The protection time (the protection capacity) is the time from material contamination until penetration occurrence on the face opposite to the contaminated one [14].

In terms of protection evaluation, the most difficult testing environment has been employed: HD (blister agent), GD (soman) and Vx (nerve agents) have been employed in 10 g/m^2 and 50 g/m^2 contamination densities for an envisaged protection time of 24 hours, as per the maximum values given in the NATO standard [13], specific to equipment most frequently to be in contact with CWAs.

Protection time determination has been made in a glove-box Jacomex workstation using no. 6 DRS system (Device for the materials verification against CWA droplets) (figure 2).

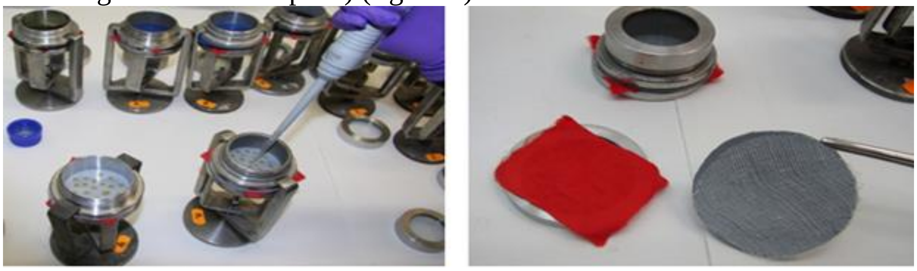


Fig. 2. Sample contamination process

CWAs diffuse through the protection equipment as the concentration gradient decreases, until they penetrate the entire thickness of the material and pass from the contaminated to the opposite part.

The emphasis of the CWA penetration through materials has been made by colorimetric analysis. The CWAs that penetrate the testing material get into contact with the indicator tissue impregnated with pH indicator (Congo Red and chloramine), chlorinates and forms hydrogen chloride that determines the colour change from red to blue, which emphasizes the material penetration by the CWA.

Representative samples from five different spots have been tested in triplicate, as following: the sample is inserted in no. 6 DRS device above a layer of indicator tissue and a layer of cotton tissue and kept at 36.5±1 °C for 15 minutes. Further, the sample is contaminated with distilled 10 or 50 g/m^2 HD/GD/Vx and again kept at 36.5±1 °C. In figure 2 is shown the process after this conditioning. The contamination moment marks the beginning of the test. Every 30 minutes the sample is verified for HD penetration. The result of the test is the lowest value obtained for the protection time determined.

Determinations on polyurea (PU) and on four-layer thicknesses of PUCs have been performed (Table 2).

Table 2
TYPES OF LAYERS USED THROUGHOUT THE STUDY

Composite material	Average thickness (mm)	Support material	Composite material	Average thickness (mm)	Support material
PU	0.55	Glove1	PU	1.75	Glove1
		Glove2			Glove2
		Glove3			Glove3
	1.20	Glove1		2.30	Glove1
		Glove2			Glove2
		Glove3			Glove3
PUC1	0.55	Glove1	PUC2	0.55	Glove1
		Glove2			Glove2
		Glove3			Glove3
	1.20	Glove1		1.20	Glove1
		Glove2			Glove2
		Glove3			Glove3
	1.75	Glove1		1.75	Glove1
		Glove2			Glove2
		Glove3			Glove3
	2.30	Glove1		2.30	Glove1
		Glove2			Glove2
		Glove3			Glove3
PUC3	0.55	Glove1	PUC4	0.55	Glove1
		Glove2			Glove2
		Glove3			Glove3
	1.20	Glove1		1.20	Glove1
		Glove2			Glove2
		Glove3			Glove3
	1.75	Glove1		1.75	Glove1
		Glove2			Glove2
		Glove3			Glove3
	2.30	Glove1		2.30	Glove1
		Glove2			Glove2
		Glove3			Glove3

Results and discussions

Various types of chemical hazards are encountered daily both at home and in industry. These substances include household chemicals, toxic industrial chemicals and CWs, and their approach depends on the tactical situation [15]: if the priority is life-saving, first-responders contamination risk must be assessed and implemented. The presence or even the potential presence of a CWA in a major incident conducts to a very challenging management of the incident due to the fact that, in the first place, the unrecognized hazards may cause first-responders to become casualties themselves. Secondly, responders capability should not be diminished due to their PE, which also may cause physical and psychological stress.

In this context, new materials for protection garment are under research worldwide against CWAs resistance. One of the most researched materials in our group has been a bromobutyl/butyl rubber, which confers a renowned 24-hour protection against CWAs (10 g/m2 HD) [14]. Furtheron, the very good results obtained for MWCNT-OH-polyurea material in terms of ballistics protection/dynamic impact [12] made the present study become of interest.

Influence of the MWCNT concentration on thermal properties of MWCNT-OH-reinforced polyurea composites

Individual PE is a key piece of clothing not only in terms of protection from hostile environments, but also as regarding heat and cold extremes. Whilst protective clothing may be designed primarily for non-thermal hazards (e.g., chemical or biological hazards), another important challenge in all protective clothing remains users comfort, i.e. thermal stress management.

Thermograms and their derivatives are given in figure 3, and the main data obtained in Table 3.

From figure 3 it has been observed that all the composites present a similar behaviour, being very stable up to ~230 ºC, with a <9% weight loss, which is very important when taking into account the polymer-textile sandwich structure for protection clothing, representing an important basis for the design of modern protective technologies and for the evaluation of individual PE materials at full-ensemble scale.

Table 3
DATA OBTAINED FROM THERMOGRAVIMETRIC ANALYSIS OF MWCNT-OH-REINFORCED POLYUREA COMPOSITES

Material	$T_{d3\%}$, °C	$T_{max\,1}$, °C	$T_{max\,2}$, °C	Weight loss, % (25-600°C)
PUC1	233	295	386	92.1
PUC2	235	294	390	92.7
PUC3	238	293	391	92.8
PUC4	242	290	395	93.8

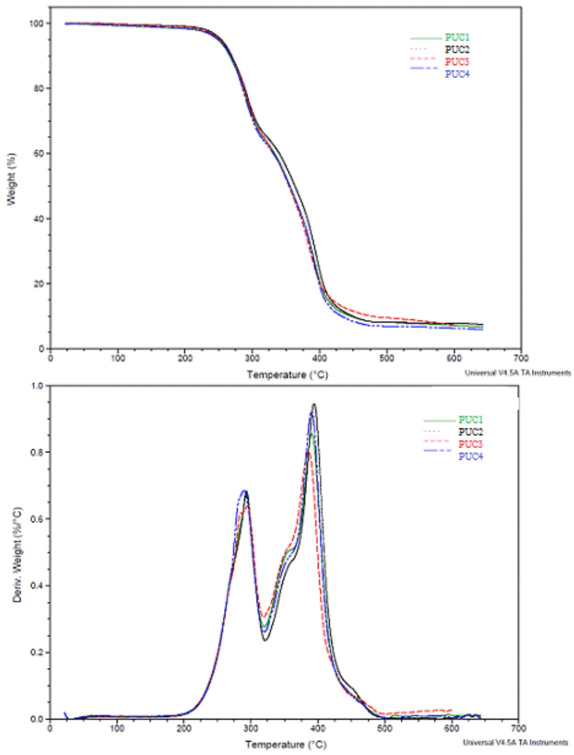
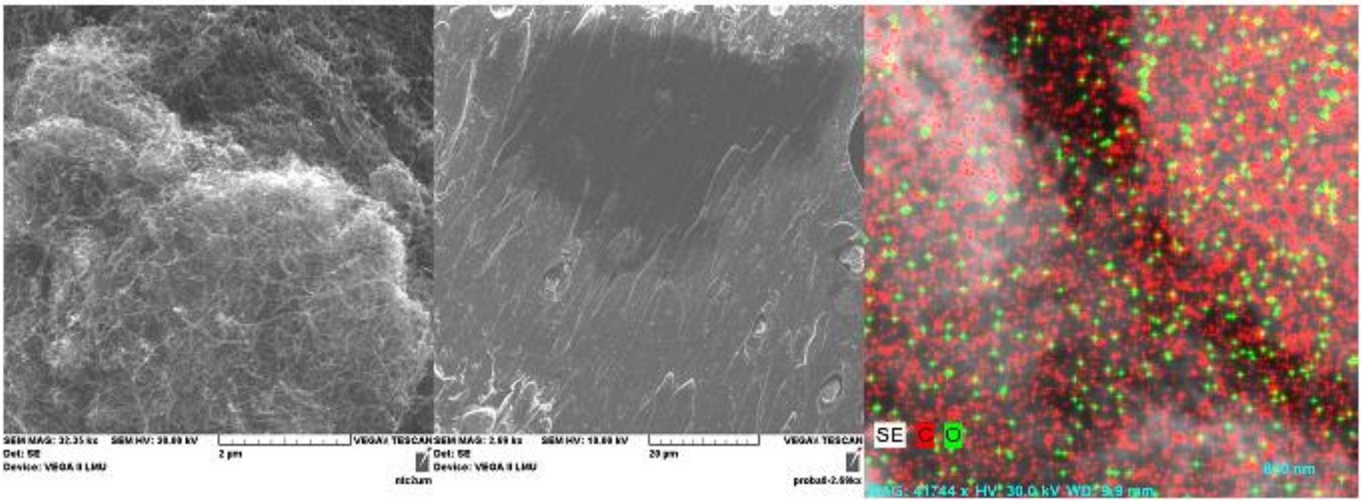


Fig. 3. Thermograms and their derivatives

Morphostructural analysis

Figure 4 gives representative microphotographs taken from the MWCNT-OH masterbatch, from the PUC layer and an EDX evaluation of the OH groups dispersed through the layer. From the analysis of the SEM micrographs obtained, one may notice a homogenous dispersion of the carbon nanotubes in the polymer matrix. The qualitative dispersion is also satisfactory, with a narrow distribution of the chemical species, this being due to the filler introduced as masterbatch in the amine used for the PUC fabrication.



a b c

Fig. 4. Microphotographs of MWCNT-OH a), PUC b) and EDX c) on PUC layer

Evaluation of the materials CBRN protection level

Evaluation of the CWAs penetration through PUC is presented in Table 4. The same results have been obtained for all the three types of support layers, which conducts, from the beginning, to a positive conclusion regarding various types of synthetic or natural polymers to be used as support materials as protective clothing against CBRN agents.

Table 4

RESULTS OBTAINED FROM MATERIALS EXPOSURE TO CWAs

Material	Layer thickness (mm)	HD		GD		Vx	
		Contamination density (g/m^2)	Protection time (hours)	Contamination density (g/m^2)	Protection time (hours)	Contamination density (g/m^2)	Protection time (hours)
PU	0.55	10	2	10	3.5	10	3
	1.20	10	3.2	10	6.4	10	6.1
	1.75	50	6	50	12	50	11
	2.30	50	10	50	16	50	15
PUC1	0.55	10	72	10	144	10	96
	1.20	10	144	10	144	10	144
	1.75	50	>168	50	>168	50	>168
	2.30	50	>168	50	>168	50	>168
PUC2	0.55	10	72	10	144	10	96
	1.20	10	144	10	>168	10	144
	1.75	50	>168	50	>168	50	>168
	2.30	50	>168	50	>168	50	>168
PUC3	0.55	10	72	10	144	10	96
	1.20	10	144	10	>168	10	144
	1.75	50	156	50	>168	50	>168
	2.30	50	>168	50	>168	50	>168
PUC4	0.55	10	60	10	120	10	72
	1.20	10	144	10	>168	10	144
	1.75	50	144	50	>168	50	>168
	2.30	50	160	50	>168	50	>168

From Table 4, one may notice the fact that the standard polyurea (PU) does not achieve the minimum requirements necessary for being used as CBRN protection material. Further, all the PUCs offer a good protection time, in agreement with [13], above 24 hours. Since, next to the protection evaluation, the study aimed at achieving also a good economical ratio, and the exposure time to the three CWAs has been prolonged for all the materials and for all the layer thicknesses. In case of the 0.55 mm-thickness, the first three materials offer at least a 72-hour protection time (against the most persistent chemical agent), while PUC4 has only a 60-hour protection time. This means that MWCNT-OH ratio in the material’s mixture is very important, lowering its ratio conducting to protection capability diminishment.

As regarding the prominence of the layer thickness, as expected, the thicker layers offer a better protection.

Economically speaking, this translates in the fact that PUC3 contains the lowest MWCNT-OH ratio where the protection time is still over one week (168 hours) in case of a 2.30 mm-layer, which reduces dramatically the cost of the product. Thus, PUC3 may be used both in CBRN individual and collective protection. PUC4 could also be of choice standing on the utility of the finite material to be employed as protection materials.

Conclusions

After having achieved very good results in terms of ballistic protection in a previous study for a MWCNT-OH-based polyurea composite, the results on determinations regarding PUC protection capacity conclude that the new solution also offers much more than the maximum protection time foreseen by the international standards (24 hours) for a contamination density of 50 g/m^2 of a persistent CWA.

Thus, next to excellent physico-chemical properties, the materials may be successfully used for the fabrication of individual and collective PE against CWAs.

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