



## HIGHLY EFFECTIVE NANOFIBERS WITH CATALYTIC CWA DEGRADATION ACTIVITY FOR CHEMICAL PROTECTION – CURRENT STATE-OF-THE ART

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**Abstract:** Current protective materials used for the development of CBRN protective suits and over garments need to fulfill two conflicting requirements: excellent protection that lasts at least 24 hours, but also high breathability and lightness. Currently employed materials, usually based on activated carbon materials, meet to some extent, these criteria. However, they still pose significant physiological burden to soldiers, and there are problems related to the secondary contamination and disposal of the used protective items. In this comprehensive review, we thoroughly analyzed recent developments regarding electrospun nanofibers and their combinations with nanoparticles that exert degradation efficiency toward chemical warfare agents. We briefly discussed various resulting protecting materials obtained in this way, compared their protective, mechanical and physiological properties and estimated their potential to be developed on an industrial scale.

**Keywords:** chemical warfare agents, protective materials, nanofibers, protection time, degradation efficacy.

### 1. INTRODUCTION

Engineered materials capable of capture and removal of chemical warfare agents (CWA), toxic industrial chemicals (TICs) and biological agents (bacteria, fungi and viruses) are highly desirable for protective textile applications. The very recent events in the beginning of the 2020, regarding the highest air pollution in Europe in the past ten years and unprecedented Covid-19 pandemics, as well as recent events in Syria regarding usage of CWA's, more than ever increased the need for the enhancement and/or development and implementation of the new types of the efficient protective materials which can be incorporated in the protective overgarments that serve to maintain the exposure to these agents as low as possible. Therefore, one of the main objectives in future will be the design of the lightweight protective composite fabrics, based on the nano-scaled supramolecular entities (particles and fibers) which will meet the following performance requirements:

- 1) Lightweightness and breathability – the resulting material should maintain or increase the overall comfort comparing to materials which are used in the current protective overgarments and protective suits;
- 2) Incorporation of active chemistry – the material should incorporate the possibility not only to retain CBW agents but also to destruct (decontaminate and disinfect) the agents in efficient manner and on the

reasonable time-scale. This will provide additional protection for the users, reduce the possibility of the cross-contamination and resolve the problems of the secondary waste storage and post-use decontamination procedures.

- 3) Reusability and durability – the resulting nano-engineered material should enable multiple usage and should possess optimal physical and mechanical properties to ensure its durability.
- 4) The material should be eco-friendly *i.e.* biodegradable and/or recyclable.

Traditional protective clothes comprise suits and over garments based on permeable materials, usually made of activated carbon liners or based on insulating materials (depending on the application rubber or other plastic and polymers). Although this kind of protective gear affords excellent protection against different kinds of toxic chemicals (especially CWAs) and biological agents, it has some major drawbacks. Some of them are bulk, increased weight and, consequently, the lack of breathability, which induces heat stress in soldiers, medical staff and other users. Moreover, these kinds of materials represent only a physical barrier against CW agents: the toxic chemicals or are retained within the material, so further steps of post-use decontamination procedures and adequate disposal are needed. Because of all stated above, there is an increasing need for the development of more effective protective materials for these purposes, which will not only represent a physical barrier against toxic chemicals, but will also perform decontamination (decomposition) of

toxic chemicals and meet all the requirements given above at the highest possible level. These kinds of products are often called “smart textiles.”

The design of the lightweight, highly breathable and self-decontaminating durable and eco-friendly material for protective suits and overgarments is achievable through the specific combination of the two main nano-scaled entities: (a) incorporation of the nanoparticulates as a carriers of active chemistry which would ensure the degradation of toxic chemicals and disinfection of pathogenic microorganisms and (b) nanofibers which would act as carriers for chemically active nanoparticles and which can be suitably modulated to ensure the optimal breathability in combination with good filtration efficiency and necessary mechanical properties of the materials.

Several chemically active nanoparticles might be useful for chemical and biological decontamination: titanium-dioxide, silver nanoparticles, magnesium-oxide aerogels, zirconium-hydroxide and cerium-oxide. Antibacterial action of the silver nanoparticles is undoubtedly and unequivocally proved in numerous studies. Titanium-dioxide is photoactive material which under UV irradiation is capable of destruction of any organic material, including both toxic chemicals and microorganisms. Beyond that, it is relatively cheap and readily available and also nontoxic [1]. But the major drawback of the TiO<sub>2</sub> is the necessity of the using UV light for its activity. Also, it has relatively low surface area and adsorption capacity comparing to for instance activated carbon which is traditionally used in the chemical protective clothing. Magnesium-oxide aerogel does not need UV irradiation for the destruction of the toxic chemicals and has relatively higher adsorption capacity, but antimicrobial activity is relatively low [2]. It was shown also that zirconium-hydroxide almost instantaneously decomposed several chemical warfare agents and also several nanocomposites based on Zr(IV) compounds exerted satisfactory antimicrobial activity [3].

Electrospun nanofibers are being designed and prepared for a variety of applications where modulation of their unique properties is used to tailor functionality of different products. Those unique properties of nanofibers include high surface area, small fiber diameter, potential to incorporate active chemistry, exceptional filtration properties, layer thinness, high permeability and breathability, and low weight. In electrospinning, a high voltage is applied to a polymer solution or melt, which overcomes the surface tension to form a charged jet. The ejected charged polymeric chains repel each other during the travel to the grounded collector and solidify in the form of thin fibers after solvent evaporation. By controlling the spinning conditions (concentration of polymeric solution, voltage, etc.), ultrafine fibers including microfibrils (>1 μm) or nanofibers (<100 nm) can be produced. In this way relatively quickly and simply a variety of different polymer materials into nanofibrous structure can be fabricated.

In this comprehensive review, we thoroughly analyzed recent developments regarding electrospun nanofibers and their combinations with nanoparticles that exert

degradation efficiency toward chemical warfare agents. We briefly discussed various resulting protecting materials obtained in this way, compared their protective, mechanical and physiological properties and estimated their potential to be developed on an industrial scale.

## 2. CHEMICALLY ACTIVE ELECTROSPUN NANOFIBERS

There are several examples of the nanofibers which bear different chemical functionalities on its surface capable of destruction of various CWA's. For instance, Ramaseshan et al. [4] produced four different types of polyvinyl chloride (PVC) nanofibers with various carriers of active chemistry including: β-cyclodextrine (BCD), o-iodobenzoic acid (IBA), and newly synthesized compound 3-carboxy-4-iodobenzoyloxy-β-cyclodextrine (3CIB). It was shown that BCD possesses high hydrolytic activity toward phosphate alkyl esters, since their hydrophobic cavity mimics the catalytic activity of hydrolase enzymes. IBA is another example of detoxification agent for organophosphorous compounds and it acts as an anionic nucleophile. In reaction with OP compounds, IBA gets converted into o-iodobenzoate anion. Oxidants such as sodium-periodate or magnesium-peroxophthalate can be used to regenerate IBA into active form. Moreover, IBA is also known to be good oxidizing agent for sulfur mustard. The PVC nanofibers were obtained by electrospinning, with the addition of BCD, IBA and 3CIB into solution. Produced nanofibers had diameters between 300 and 450 nm, and the porosity of all membranes was greater than 80% which show that membranes would allow moisture exchange. Hydrolytic activity of the nanofibers was tested using spectrophotometric method and paraoxon as a model compound. The highest activity toward paraoxon hydrolysis showed membrane with 3CIB derivative incorporated, and it removed paraoxon 11.5 times faster than activated carbon by adsorption, which is promising result.

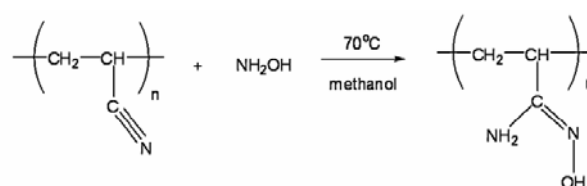
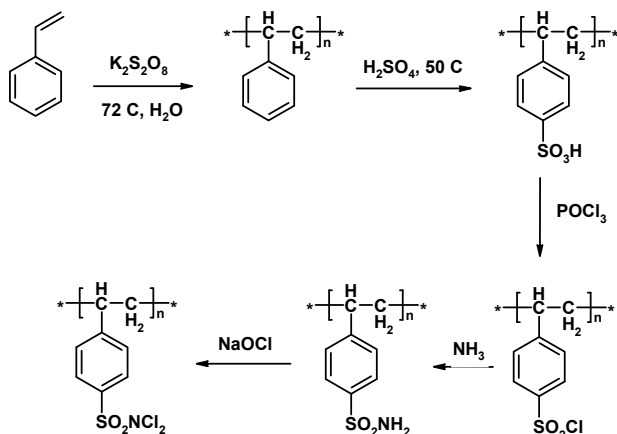


Figure 1. Oximation of PAN fibers.

Chen et al. [5] produced polyacrylonitrile nanofibers (PAN) and modified them by oximation with hydroxylamine to produce polyacrylamidoxime (PAAO) nanofibers as detoxifying protective fabrics, Figure 1. The obtained fibers had diameters from 250 to 500 nm. The hydrolytic activity of the nanofibers was investigated using <sup>31</sup>P MAS NMR and diisopropylfluorophosphate (DFP) as a model compound. The apparent second-order rate constant, for the DFP hydrolysis was 10<sup>-6</sup> s<sup>-1</sup>mg<sup>-1</sup>. The hydrolytic degradation of DFP occurs only in the presence of water, since dried fibers did not degrade DFP. The authors concluded that water serves as a medium to promote the nucleophilic action of the amidoxime groups

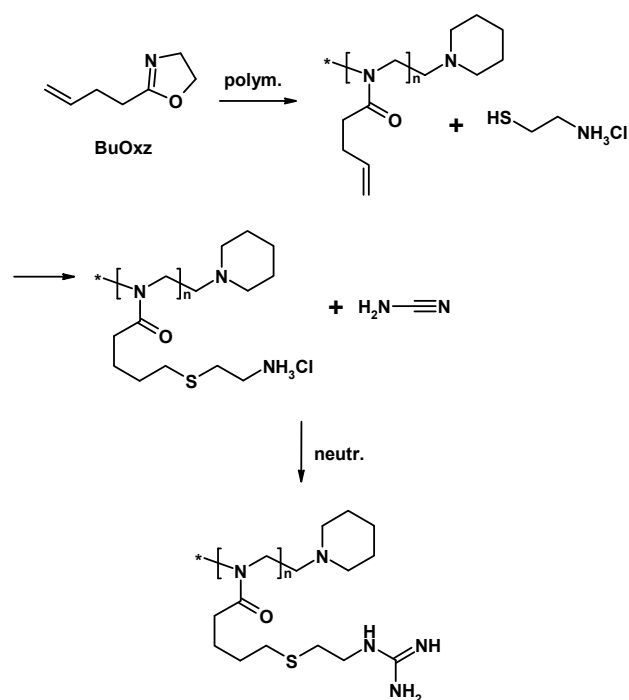
in the fibers by facilitating proton transfer and stabilizing the transition state.

Maddak and Azimi [6] produced nanofibers by combining the two polymers, *N,N*-dichloropolystyrene, as a donor of active chlorine species and polystyrene by electrospinning. The *N,N*-dichloropolystyrene was synthesized from polystyrene in five steps, that included sulfonation of polystyrene by sulfuric acid, chlorination with  $\text{POCl}_3$ , amidification and chlorination by hypochlorite (Figure 2). The obtained nanofibers had diameters between 160 and 300 nm. The decomposition reaction of 2-CEES on the nanofibers was monitored by GC-MS. Very fast decomposition reaction of 2-CEES on the nanofibers was observed – the total amount of 2-CEES was decomposed in the timeframe of 7 minutes, with the main products of decomposition being ethyl vinyl sulfone, (2-chloroethyl)ethyl sulfone, (2-chloroethyl)ethylsulfoxide, depending on the ratio between 2-CEES and active chlorine species. The amount of active chlorine species in the nanofibers did not varied significantly during six months after production, yielding the stable protective materials.



**Figure 2.** Synthesis of *N,N*-dichloropolystyrene sulfonamide.

Ying and coauthors made a versatile nanofibers combined of guanidine functionalized poly(2-(3-butenyl)-2-oxazoline and Nylon-6,6 polymers by coelectrospinning [7]. Nylon was chosen as a versatile material which is thin and flexible, and also has a high durability and toughness. However, it has a difficulty of introducing functional groups and therefore has a limited application in various specialized fields. Polyoxazolines were chosen because they represent a structural variant of nylon with amide functional groups in the side chains, which can be easily functionalized. Firstly, the poly(2-(3-butenyl)-2-oxazoline was synthesized, then amine groups were introduced using thiolene click chemistry, followed by guanidization, Figure 3. Guanidine as functional reactive group was chosen, due to its strong basicity, with pKa around 13.6, and can be used as a catalyst for decomposition of organophosphates. Although functionally very reactive, the G-PBuOxz polymer has poor physical properties, forming a gel which is not able to yield nanofibers upon electrospinning.



**Figure 3.** Preparation and guanidization of poly(2-(3-butenyl)-2-oxazoline

However, the mixture of Nylon-66 and G-PBuOxz was electrospun successfully yielding the nanofibers without any notable phase separation. The obtained nanofibers were very effective for the destruction of DFP.

In another work, non-woven nanofiber webs were produced using polyacrylonitrile (PAN) suitably modified by ethylenediamine using chemical vapor deposition process (CVD) to introduce available and hydrolytically active amino-groups into polymer [8]. CVD method may provide several benefits over solvent based treatment of the substrates, because it creates no waste and residues, and it doesn't affect the target material during modification. It is also able to produce uniform coating on the various substrates. In this case, by using various amines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, and ethanolamine and various temperatures for CVD process, several amino-modified PAN nanofibers were produced. Their ability to degrade DFP was investigated by NMR spectroscopy. The fibers which were produced with CVD treatment of PAN with ethylenediamine at 120 °C showed the best DFP degradation efficiency.

### 3. ELECTROSPUN NANOFIBERS WITH CHEMICALLY ACTIVE NANOPARTICLES

Many studies investigated the usage of magnesium-oxide (MgO) nanoparticles as carriers of active chemistry in permeable protective materials. They are cheap, easily made and non-toxic and above all, don't require the presence of UV/Vis light to initiate decomposition reaction, which is needed in case of titanium-dioxide nanoparticles.

Sundarrajan and Ramakrishna [9] prepared nanofibers based on the three different polymers: polyvinylchloride (PVC), poly(vinylidene fluoride-co-hexafluoropropylene (PVDF) and polysulfone (PS) and MgO nanoparticles. Firstly, they prepared nanocrystalline MgO and dispersed into solution of polymers for the electrospinning process. The loading of the MgO nanoparticles in the resulting nanofibers was around 30 wt %. The hydrolytic activity of the nanofibers with MgO nanoparticles was investigated by UV-Vis spectrophotometric method using paraoxone as a model compound. The order of reactivity of the membranes was PVC-MgO < PVDF < PSU < PVDF-MgO < PSU-MgO. The PSU-MgO nanoparticles were around two times faster in decomposition of paraoxone, comparing to the activated carbon for the adsorption. Yet the MgO nanoparticles tested in bulk were more active comparing to the PSU-MgO nanofibers which contained the same amount of MgO. The complete decomposition of paraoxone with PSU-MgO nanofibers was achieved after 200 minutes.

In another work by Liu et al. [10], the MgO nanoparticles were *in situ* grown on the surface of poly(m-phenylene isophthalamide), (PMIA), producing a flexible and breathable fabric for CWA's detoxification. The percentage of MgO on PMIA nanofibers was around 11%. The electrospun PMIA nanofibers were dipped into solution of MgSO<sub>4</sub>, which was hydrolyzed to Mg(OH)<sub>2</sub>, and the fibers were subsequently annealed at 350°C. The PMIA polymer has a high glass transition temperature, so it would not decompose or carbonize below this temperature used for annealing. The functional groups of PMIA would also easily form weak intermolecular interactions with MgO due to the lone pairs on oxygen atoms of PMIA. The degradation efficiency was tested using 2-CEES, a sulfur mustard surrogate by GC-MS. The degradation ability was obvious but relatively slow: around 70% of the 2-CEES was destructed after 20 h of reaction time.

Dadvar et al. [11] investigated the ability of activated carbon nanofibers embedded with MgO or Al<sub>2</sub>O<sub>3</sub> nanoparticles to decompose 2-CEES. They used commercially available nanoparticles; MgO was in crystalline form, with particle size of 4-8 nm, while Al<sub>2</sub>O<sub>3</sub> was amorphous. The specific surface area of both types of nanoparticles was between 200 and 600 m<sup>2</sup>/g. Firstly, they made MgO or Al<sub>2</sub>O<sub>3</sub> polyacrylonitrile nanofibers by electrospinning and subjected them further to the process of carbonization and activation. The nanofibers with MgO and Al<sub>2</sub>O<sub>3</sub> which had higher surface area showed better decontamination efficiency. Around 80% of 2-CEES was removed after 120 minutes of reaction time. Authors concluded that faster decontamination and a higher decomposition yield is related to both higher amounts of nanoparticles embedded in the nanofibers, but is also related with increase in the available reactive sites as a result of higher number of bigger pores.

Ramaseshan and Ramakrishna [12] made polyvinyl-pyrrolidone nanofibers (PVP) incorporated with zinc-titanate nanoparticles for the destruction of CWA's. They produced zinc-titanate nanofibers with sol-gel approach using a polymer binder PVP. The precursors for ZnO and

TiO<sub>2</sub> were titanium-tetraisopropoxide and zinc-acetate, dissolved in ethanol and in the presence of acetic acid the PVP polymer was dissolved. Different ratios of zinc and titanium were used. This mixture was electrospun to obtain the corresponding nanofibers. The nanofibers collected as random mats were annealed at different temperatures ranging from 300 to 700 °C, and cooled with the controlled temperature rate. The BET surface area of the annealed nanofibers was 90-130 m<sup>2</sup>/g. The only drawback of this approach is that nanofibers became very brittle after annealing. The nanofibers with zinc/titanium ratio of 4:6 annealed at 700 °C showed the highest decomposition efficacy both for paraoxon and 2-CEES; around 87 % of paraoxon was degraded in the first 50 minutes of the reaction, while 67% of 2-CEES was degraded in the first 10 minutes of the reaction. The products of reaction of zinc titanate against the simulants are identified and are found to be relatively harmless. The possibility of replacement of conventional-activated carbon by electrospun ceramic nanofibers for face masks and protective clothing is proposed.

Ryu et al. produced lightweight nanofibrous assemblies with high protection ability against CWA's using laminated outer and inner layer based on nanofiber composite materials [13]. The outer layer was composed of meta-aramid (Nomex) nanofibers and CWA commercially available adsorbents, MgO fine powder of 325 mesh (Sigma Aldrich) and polyoxometalate ammonium phosphomolybdate hydrate, (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> x nH<sub>2</sub>O. These adsorbents were added to the electrospun Nomex nanofibers by electrospraying process. The fibers were then thermally treated at 300 °C, above the glass transition of NOMex, then treated with Unidyne to obtain oleophobic properties. The inner layer was made from polyamide 66 nanofibers and also included above mentioned sorbents for CWA's. The outer layer possessed high mechanical strength and an amphiphobic surface, capable of repelling liquid CWA's. The inner layer exhibited low permeability to gaseous CWA's and a high permeability to water vapour. Several combination of inner and outer layers were merged by glue spraying to produce different protective materials which contained 1 to 7 different layers. The permeability of the assembled protective materials were tested according to TOP 08-2-501 standard procedure which determines the permeability for challenge agents DMMP and 2-CEES. The highest protective ability had the material which consisted of 2 outer and 4 inner layers and exhibited permeability of 362.53 μg/cm<sup>2</sup> for 2-CEES and 126.30 μg/cm<sup>2</sup> for DMMP which is comparable to the permeability of conventional protective clothes. Authors concluded that these results indicate that the assemblies based on nanofibrous composites can be used to make lighter protective clothing materials than those currently available. Furthermore, the assembly with two outer and six inner sheets, which had comparable weight density to that of the reference protective clothing, exhibited improved protection ability against the simulants.

Many studies investigated the usage of metal organic frameworks (MOF) as carriers of active chemistry on different types of nanofibers for the destruction of toxic chemicals. The vast majority of materials in this area

focus on attaching MOF particles on fibers through covalent attachment or electrospinning polymers containing MOFs in the bulk solution. More recent efforts have focused on *in situ* techniques, where MOF particles are directly grown on the surface of the polymer rather than processing a polymer mixture containing preformed MOF powders into fibers.

**Table 1.** Novel nanofibers for CWA protection.

Ref.	Nanofiber	Active group	Test agent	Activity/protection
[4]	PVC	BCD, IBA	Paraoxon	11.5 x faster than active carbon
[5]	PAN	-oxime	DFP	$10^{-6} \text{ mg}^{-1} \text{ s}^{-1}$
[6]	PS, N,N-diCIPS	N-chloro	2-CEES	Total decomposition in 7 min
[7]	Guanidine functionalised polyoxazoline	-guanidin	DFP	approx. 60% removal in 2h
[8]	PAN	Ethylene Diamine	DFP	Total decomposition in 24 h
[9]	PVC, PVDF, PS	MgO, 30%	Paraoxon	2x faster than active carbon
[10]	PMIA	MgO, 11%	2-CEES	70% for 20h
[11]	PAN	MgO, Al <sub>2</sub> O <sub>3</sub> carbonisation	2-CEES	80% for 120 min
[12]	PVP	ZnTiO <sub>3</sub>	Paraoxon 2-CEES	87% in 50 min 67% in 10 min
[13]	Nomex Polyamide 66	MgO, POM	DMMP 2-CEES	Similar to available PPE

#### 4. CONCLUSION

In the Table 1, all that was discussed above is summarized. It seems that nanofibers with organic functional groups reactive toward CWA's are good strategy for designing smart protective materials. Nanofibers with incorporated IBA and also dichloro modified polystyrene showed exceptional activity for destruction of the nerve and blister agents' simulants. On contrary, majority of nanofibers with nanoparticles incorporated whether in bulk or on their surface showed comparatively lower, but still promising degradation of the challenge agents. However, they have the advantage of reusability comparing to the nanofibers which directly react with the agents. In conclusion, both types of nanofibers show promising potential for the development of novel protective materials and personal protective equipment, and we should expect design of novel promising materials in the foreseeable future.

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