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# POLYMER COMPOSITE MATERIALS AND APPLICATIONS FOR CHEMICAL PROTECTION EQUIPMENTS

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*Abstrac:* The polymer composite materials properties are clearly determined by their constituent properties and by the micro-structural configuration.

Additives and modifiers ingredients can expand the usefulness of the polymeric matrix, enhance the processability or extend composite durability. The fibres are mainly responsible for the performance changing (strength and stiffness properties). The least structurally demanding cases is the arrangement of fibres randomly in polymeric matrix, when equal strength is achieved in all directions. Fibre reinforced polymer materials can be successfully used in a wide range of applications and can significantly improve the characteristics of chemical protection equipments and foster the development of new ones with superior features.

### Keywords: polymer composite materials, chemical protection

### 1. Introduction

Chemical weapons have a longer history. In general the production of chemical weapons is not very difficult. International treaties have imposed restraints on the development and use of these weapons but there are still countries and terrorists seeking possession of such weapons.

When submitted to the danger of chemical warfare agents, protective measures must be taken, in order to avoid both military and civilian contamination and to reduce casualties. Another reason for adopting protective measures is relative with possible accidents at chemical plants (resulting toxic industrial chemicals, or TICs). Therefore, continuous research is performed in order to improve the parameters of the protection equipments. In this respect we studied the possibility of using new materials for protection as the polymer composite materials.

Composite materials are made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with net superior characteristics different from the individual components. The individual components remainseparate and distinct within the finished structure.

Fibre-reinforced composite materials have gained recognition in high- performance products that need to be lightweight and also strong enough to resist at violent loading conditions, such as: racing car bodies, boat hulls, aerospace components, etc.

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#### 2. Polymer composite materials (PCMs)

The PCMs considered are composed of a polymer matrix reinforced with fibres. The polymer matrix is polyurea and the considered fibres are modified carbon nanotubes and graphene oxide. Fibre reinforced polymer materials have been used successfully for many years in a wide range of applications, predominantly in the aerospace and automotive industries. The PCMs mechanical and physical properties are clearly determined by their constituent properties and by the microstructural configuration. While the fibres are mainly responsible for strength and stiffness properties, the polymeric matrix contributes to stress transfer and provides microclimate protection. In addition, fillers are used to improve performance, imparting benefits as shrinkage control, surface smoothness and crack resistance.

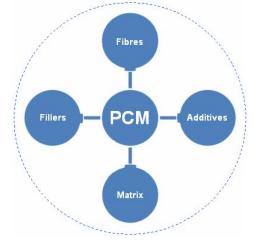


Figure 1 – PCM components

Additives and modifiers ingredients can expand the usefulness of the polymeric matrix, enhance their processability or extend composite durability (Fig 1). The reinforcing of a polymeric matrix with high strength and modulus fibres utilizes the viscoelastic displacement of the matrix under stress to transfer the load to the fibre; this result in a high strength, high modulus composite material. The aim of the combination is to produce a two phase material in which the primary phase, that determines stiffness, is in the form of fibres and is well dispersed and bonded and protected by a secondary phase, the polymeric matrix.

### 2.1 PCMs constituents

The key constituents that have been considered for achieving PCMs are:

grapheme oxide, functionalized carbon nanotubes and polyurea.

### Graphene oxide (GO)

In the past few years, various kinds of polymer/GO nanocomposites with remarkably enhance mechanical properties net superior to usual composites, have been reported. Therefore, more attention has been drawn to GO as potential reinforcement materials in the generation of polymer composite materials.

The individual (1 layer) platelets of GO have an effective Young's modulus of

207 GPa  $\pm$  11%, indicating one of the strongest materials ever measured. The promising properties, together with the ease of processing make GO-based materials ideal candidates for incorporation into a variety of functional materials.

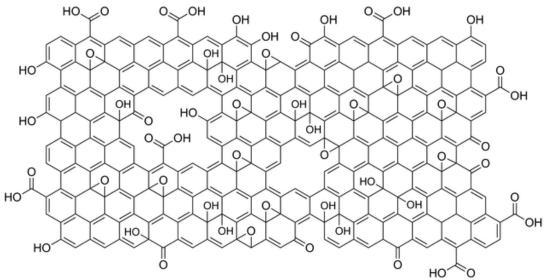


Figure 2 – Model of graphene oxide (GO)

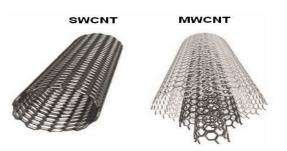
Polymer nanocomposites with GO- derived materials as filler have shown dramatic improvements in properties such as elastic modulus. tensile strength. electrical conductivity, and thermal stability, even at very low concentration of GO (0.3 wt%). The improvement observed in the mechanical properties of the polymers is suggested to arise from the good mechanical interaction between the polymer and small amounts of GO that provides better load-transfer between the matrix and the fibre.

The technology for GO synthesis was based on Hummers method. GO micro-flakes were prepared from graphite micro-flakes by oxidative strategy with mixed acid media which offered high recovery of graphite oxides whose micro- flake dimensions were approximate those of the original graphite crystals.

The synthesized GO was characterised by FT-IR, TGA, XPS, Raman spectroscopy and SEM.

## Carbon nanotubes (CNTs)

CNTs are long cylinders of covalently bonded carbon atoms, which possess extraordinary electronic and mechanical properties. There are two basic types of CNTs: single-wall carbon nanotubes (SWCNTs) which are the fundamental cylindrical structure and multi-wall carbon nanotubes (MWCNTs) which are made of coaxial cylinders (Fig. 3), having interlayer spacing close to that of the interlayer distance in graphite (0.34 nm). These structures cylindrical are only few nanometre in diameter, but the cylinder can be tens of microns long, with most end capped with half of a fullerene molecule. M. Endo first discovered it in 1978, as part of his Ph.D. work at the University of Orleans in France, but real interest in CNTs started when Iijima first reported it in 1991. The field thrives after that and the first polymer composites using CNTs as reinforcing components were reported in 1994 by Ajayan et al.



The functionalized carbon nanotubes were preferred due to their better coupling with polymeric matrix through functional groups (-COOH; -NH2). Therefore were synthesized and characterised by FT-IR, TGA, XPS and Raman spectroscopy.

#### Polyurea

Polyurea is created by the chemical reaction (polyaddition) between a di- isocyanate (NCO-R-NCO) and a polyamine (NH2-R-NH2), without the aid of a catalyst or an additional cross linker.

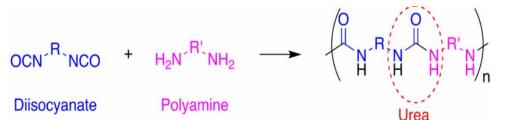


Figure 4 - General reaction for forming a polyurea chain

The characteristics of polyurea are suitable as polymer matrix for PCMs and appropriated for industrial production of protective equipments:

No VOC's (volatile organic compounds);

• Polyurea coatings are flexible in all weather conditions;

✤ Processing temperature: -30°C...+60°C;

• Holds up at low temperatures (- $60^{\circ}$ C);

 ✤ Excellent heat resistance up to 130°C, short-term up to 220°C;

✤ Fast reaction (sprayed surface can be further treated after just 1 hour);

 ✤ Applied thickness ranging from only 1 to 100 mm;

Stretches 3 times its length without breaking;

- $\bullet$  UV stability;
- ✤ Seamless and elastic;

♦ Waterproof barrier (acts as a seal) and hydrolysis stable;

Solvent-free so not explosive or an environmental hazard;

Protects high wear areas;

Dent and scratch resistant;

✤ Excellent bonding with other materials;

✤ Good chemical resistance;

✤ Safe even for potable water containers;

✤ Long lasting;

Slip and skid resistant;

✤ "Green technology" (no solvents, 100% reaction);

Simple machine processing due to low viscosities;

✤ Variety of base colours stable even in prolonged direct sunlight;

Easy to clean.

## **2.2. PCMs areas of applications**

The progress beyond the state of the art, for applications with market potential, consists in producing of PCMs with excellent chemical and mechanical resistance. Different types of reinforcement fibres (hybrid composites) and different thickness can be expressly used for specialised applications of PCMs, for the following purposes: hazardous chemicals protection; outer cover for CBRN collective protection tents (COLPRO); CBRN individual protection equipment, etc.

## 3. Conclusions

CBRN protection equipment of modern armed forces includes more and more efficient protection elements. The polymer composite material presented in this paper able to dramatically is improve the protection characteristics of existing equipments and will foster the development of new ones with better characteristics (reduced mass. advance protection capabilities), due to excellent mechanical

properties and resistance to hazardous chemicals. Along the protective characteristics of PCMs, as benefit, these can be produced in specific shapes and dimensions, with the purpose of using it for production of protection equipments.

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#### References

- [1] Y.G. Yang, C.M. Chen, Y.F. W, Q.H. Yang, M.Z. Wang, *Oxidized graphene and graphene based polymer composites*, New Carbon Mater, 23 (3), pp. 193–200, 2008.
- [2] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *The chemistry of graphene oxide*, Chem. Soc. Rev., 39, 228–240, 2010.
- [3] K.E. Prasad, B. Das, U. Maitra, U. Ramamurty, C.N.R. Rao, *Extraordinary* synergy in the mechanical properties of polymer matrix composites reinforced with 2 nanocarbons, Proc Nat Acad Sci, 106 (32), pp. 13186–13189, 2009.
- [4] C.M. Damian, A.M. Pandele, C. Andronescu, A. Ghebaur, S.A. Garea, H. Iovu, Epoxy- Based Nanocomposites Reinforced with New Amino Functionalized Multi-Walled Carbon Nanotubes, Fullerenes, Nanotubes and Carbon Nanostructures, 19 (3), 197-209, 2011.