PREPARATION AND PROPERTIES OF MICRO- AND NANOFILLED POLYMER COMPOSITES ON TEXTILES

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Abstract

During the development of suitable radar absorbing material (RAM) various options were tested in order to investigate their interaction with electromagnetic wave. Several different carbon micro- and nanofillers were incorporated into a polymer matrix and composites were prepared at various filler percentages. Carbon nanotubes (CNTs), carbon black and micronised graphite particles were used as fillers. Composites were prepared either as thin films on nonwoven textiles or filled into 3D structures – polyurethane (PU) foams and 3D-polyester textiles.

The ability of carbon-filled structures to attenuate an electromagnetic wave was investigated in the microwave range from 2 to 18 GHz. Spectral insertion loss of reflection ILR of samples was determined.

Keywords: nanotubes, micronised graphite, 3D textiles, radar absorbing materials

1. INTRODUCTION

This article presents the most relevant results obtained while solving the Ministry of Defence research project VOJAN – Nanotechnologies for military applications. Project aim is to assess the possibility of nanomaterial utilization in protection of military forces of the Army of the Czech Republic on the basis of both, theoretical and experimental research work. The objective is to study nanostructures and nanocomposite thin films on flexible substrates with respect to their utilization as radar absorbing materials (RAMs). In earlier stages of the project an extensive review has been made, summarizing the requirements on camouflage means (Basic overview could be found in [1].) and material properties.

The most effective way to conceal an object is to place a reflecting or absorbing surface between the object and a source of electromagnetic radiation. Conventional RAMs exhibit excellent absorbing properties, they are, however, often limited by their dimensions, high weight and limited mobility. And mobility as well as flexibility is one of most crucial demands on modern camouflage means. Therefore project concentrates on preparing a RAM on a flexible substrate, while achieving desired absorbing properties. The review recommends concentrating on preparation of thin polymer composite films on textiles and other flexible structures, such as foils or foams. Also recommends carbon microparticles and nanoparticles as fillers. This is in agreement with [2]. RAM with CNTs were already reported e.g. in [3], [4].

Included in this article are the very first results, obtained during second year (out of four) of the project and therefore it is necessary to see them mainly as a base for further work. However, even these preliminary results demonstrate that nanocomposites and nanostructures on textiles actually may be a reasonable equivalent to conventional materials.

2. EXPERIMENTAL

2.1 Materials

As a substrate for RAM composites a 100% polyester 3D textile is used. 3D textile is a type of knitted fabric, where not only length and width, but also height could be determined. It is formed by linking two separate
fabrics by a network of perpendicular threads. Right side, wrong side and profile of 3D textile is in Fig. 1. 3D textile is exceptionally air permeable, non absorbent, flexible, easily shapeable and very light (250 g/m² for a 3 mm thick textile). For this work 3D textile high 3 mm and 6 mm was used.

As fillers two different types of microparticles were used. First is micronised natural graphite CR2 995 produced by Graphite Týn. Graphite CR2 995 contains over 99.5 % of carbon (typically 99.7 %), less than 0.5 % of ash particles and less than 0.4 % moisture. Average particle size is between 3.5 – 5.5 µm. Specific surface area is 13,0 m²/g and apparent density is 160 g/l. Apart from carbon the CR2 995 contains also silicon - 1500 ppm, calcium - 450 ppm, aluminium - 250 ppm, iron - 200 ppm and magnesium - 100 ppm.

Second microfiller was carbon black, Pigmasset BD-T. Average particle size is 1.8 µm. Micrograph analysis showed, that Pigmasset carbon forms clusters which needs to be carefully dispersed before incorporating into the matrix.

Carbon nanotubes produced by Nanocyl (Belgium) were used as nanofiller. CNTs were used in a form of aqueous suspension sold under the trade name AquaCyl. CNTs were prepared by catalytic CVD, purified to contain 90 % of carbon, the rest are metal oxides. Diameter is 10 nm and average length is 1,5 µm. Specific surface area is 250 – 300 m²/g. After purification CNTs are dispersed in deionised water. Good dispersion is achieved by using anionic surfactants. Concentration of CNTs in the suspension is 1%. AquaCyl was chosen because of its low impact on environment, reasonable price and especially for easy processability.

As a matrix Axilat 942 was used. It is the aqueous thermoreactive dispersion of styrene acrylate copolymer, anionactive. It is produced by Hexion Specialty Chemicals. Axilat is miscible with water (and therefore also with AquaCyl suspension) and forms films easily. Optimum crosslinking temperature is approx. 110°C to 140°C. Films are transparent, resistant to water and to organic solvents, but quite soft.

Micro- or nanofillers were dispersed into matrix and filled into a 3D textile by impregnation using laboratory foulard Mathis at the process speed of 10 m/s. Impregnated textiles were dried in the oven at the temperature of 130°C.

### 2.2 Measurement

The ability of composites to attenuate the electromagnetic wave was determined by measurements in the range from 2 GHz to 18.6 GHz. It corresponds with the working range of ground surveillance radars. Vector analyzer Anritsu 37369C with integrated transmitter and receiver was used. Two horns are connected to the analyzer, their distance is 60 cm and halfway between them is a sample holder. This arrangement is regarded as a free space. Metal desk, which is considered to be 100% reflective is attached to the holder.
and is a reference for reflectivity measurements. Absorbing sample and metal plate are placed in the holder and the reflection is measured. From obtained values insertion loss for reflection ILR is determined according to the formula on the left. \( S_{11\text{sample}} \) is a coefficient of reflection for the absorbing sample and \( S_{11\text{ref}} \) is coefficient of reflection for the metal plate reference. Further details can be found in [5] or [6].

3. RESULTS

Microcomposites with micronised graphite were prepared at different concentrations and filled into a 3D textile 3 mm and 6 mm high. Fig.2. shows spectral dependence of the insertion loss for reflection ILR of microcomposites in 3 mm textile. Filler concentrations are given in the legend. Best results are obtained for lowest filler concentrations. Same samples prepared on 6mm textile exhibited similar results, only the wavelength where the maximum loss occurs is different – 3 cm and 4.5 cm for 3 mm and 6 mm textile, respectively.

![Fig. 2 Spectral dependence of ILR for 3 mm 3D textile filled with micronised graphite with different weight concentrations.](image-url)
Fig. 3. shows the same parameters for microcomposites with carbon black in 3 mm 3D textile. Best results were obtained for filler concentration of 15 wt.% and for all higher concentrations the ILR was lower and had more or less the same values. This suggests that the percolation threshold for carbon black occurs approx. at the concentration of 15 wt.% or even lower. For micronized graphite the percolation threshold is lower than 22 wt.%. Further work would be focused on samples with lower concentrations.

Fig. 4. Spectral dependence of ILR for 3 mm 3D textile filled with carbon nanotubes with different concentrations.
In Fig. 4, the spectral dependences obtained on nanocomposites in 3 mm 3D textile are plotted. On 6 mm textile the results for same concentrations were similar. ILR is better for higher concentrations, because we are under the percolation threshold and in further work the concentration must be increased. The loss maximum is 2.5 dB and 2.75 dB for 3 mm and 6 mm textile, respectively. Compared to micronized graphite (18 dB) it seems to be negative result, but the CNTs concentration is 20 times lower than that of micronized graphite. The ILR should also significantly improve once we find the percolation threshold for CNTs. E.g. in [7] the best absorption properties were observed at the CNT concentration of 4 wt.%

Sandwich structures were prepared from microcomposites with the micronized graphite and measured the same way as monostructures. Sandwich structures contain two layers, first one is 3D textile filled with micronized graphite and its thickness was 3 mm. Second one was just 3D textile without any filler, its thickness was either 3 mm, 6 mm and 6+3 mm (actually two layers of empty 3D textile without filler and different thickness). In Fig. 5, ILR characteristics of a monolayer with 22 wt. % of micronized graphite and three individual sandwiches are shown. The changes in the spectral dependencies are quite hard to describe due to the complexity of the problem. The sample thickness clearly caused the shift of the IRL maximum, but the thicknesses of individual layers in the sandwich structure as well as thickness of the whole structure are just two of the parameters to consider. So far we cannot predict the shape of the IRL curve by mathematical equation and best sandwich layer has to be found experimentally. This will be aim of our future work.

4. CONCLUSION

Results obtained in the second year of research project VOJAN so far confirm that micro- and nanoparticles are suitable fillers for micro and nanocomposite RAM materials. Although results from microwave measurements must be regarded only as informative, it is clear that with these materials a convenient RAM could be prepared. The following work will be focused on finding the most suitable filler concentrations. In case of micronized graphite it means concentrations lower than 22 wt% and for carbon black concentrations...
lower than 15 wt%. Concentration of CNTs should be higher than 1 wt%. Sandwich multilayers seem to be a perspective candidates for high quality radar absorbing structures as well.

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LITERATURE