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Preparation and electromagnetic properties of epoxy/organoclay/MWCNT/gold nanocomposites

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Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc, Corresponding Member of the Bulgarian Academy of Sciences

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This study is concerned with preparation methods and electromagnetic properties of epoxy/organoclay/MWCNT/Au nanocomposites. Nanofillers were prepared by using an impregnation method and characterized through TEM. The nanocomposites were prepared using *in-situ* polymerization technique. Results of this research show a synergistic effect between MWCNTs and AuNPs and improved electromagnetic shield properties of the nanocomposites.

Keywords: preparation, gold nanoparticles, organoclay, MWCNT, electromagnetic properties

INTRODUCTION

A typical gold nanoparticle synthesis involves chemical reduction of gold chloride using sodium borohydride and sodium citrate to produce particles of 2–10 and 12–100 nm size, respectively [1]. To support gold nanoparticles on a stable inorganic or organic matrix is a prime requirement for applications such as catalysis. Varieties of supports as SiO_2, TiO_2, Al_2O_3, Fe_2O_3, carbon, clay, and polymer for stabilizing gold nanoparticles have been reported [2–5]. Zhang *et al.* [6] have reported decoration of gold nanoparticles on layered silicates. They suggest a simple wet chemical method to synthesize clay-APTES-Au nanocomposites where 3-aminopropyl-triethoxysilane (APTES) acts as the linkage. APTES silane terminal forms bonds with the clay surface, while the $–NH_2$ terminal bonds interact with gold nanoparticles. Patel *et al.* [7] suggest a method for preparation of gold nanoparticles anchored on surfactant-intercalated montmorillonite (MMT). They have used two approaches to synthesize gold nanoparticles. One of the methods involves gold nanoparticle synthesis by reduction of gold salt in hexadecyl trimethyl ammonium bromide (HDTA) and dioctadecyl dimethyl ammonium chloride (DODA) followed by exchange of HDTA and DODA solution containing gold nanoparticles into MMT. In the second approach, HDTA and DODA with gold salt is exchanged with MMT and then reduced to obtain gold nanoparticles.

In the last years, most of the studies of Au-CNT nanocomposites are focused on sensors applications [8–11]. Carbon nanofillers show high wave absorption properties, however, addition of carbon nanotubes (CNT) to polymer nanocomposites decreases the absorption effect [12, 13]. A combination of carbon nanotubes with gold nanoparticles in nanocomposite materials may lead to synergistic effects between the two nanofillers.

EXPERIMENTAL

Materials

Clay Cloisite 30B (Southern Clay Products, Inc.), organically modified with methyltallow bis-2-hydroxyethyl quaternary ammonium chloride (MT2EtOH) was used as a substrate for gold nanoparticle synthesis. Tetrachloroaurate trihydrate ($HAuCl_4.3H_2O$) from Sigma-Aldrich was the precursor for the synthesis of gold nanoparticles. Epoxy resin prepolymer Epilox T 19-38/500 (liquid oligomer, η = 450−550 mPa.s at 25 °C) and amine hardener Epilox H 10–30 (η = 200−300 mPa.s at 25 °C) were purchased from Leuna-Harze GmbH (Germany) and used as received.

Preparation methods for nanofillers, nanodispersions, and nanocomposites

A variation of the wet impregnation method for ‘decoration’ of clay with gold nanoparticles is proposed using an aqueous solution of $HAuCl_4$ as a precursor. Quaternary alkylammonium MT2EtOH as the organoclay intercalate was used both to attach gold nanoparticles onto organoclay and as a reducing agent. A $HAuCl_4$ solution in distilled water (3.35 g, 0.00017 mol $HAuCl_4$) was prepared with a concentration of 1.73 wt%. After that the $HAuCl_4$ aqueous solution was mixed with 1.71 g clay for 30 min. The resulting mixture was further dried in an

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oven at 80 °C for 8 h and then irradiated for several hours using UV light until the color of the treated clay turned to dark gray. Thus, both the organoclay modifier and the UV treatment promoted the subsequent reduction of the gold cations to neutral gold atoms forming gold nanoparticles on the clay platelets. The result of this synthesis was clay decorated with 1.92 wt% of gold nanoparticles with an average size ranged from 5 to 150 nm as described in detail in our previous work [14].

For preparation of ternary nanodispersions an appropriate amount of AuNPs/clay was added to the liquid epoxy resin oligomer and the mixture was homogenized for 30 min by mechanical mixing at 9000 rpm followed by a 30-min ultrasonication treatment at 250 W. The obtained gold/clay/epoxy nanodispersions were then degassed in a vacuum oven for 1 h at 90 °C and cooled to 20 °C. The respective amount of MWCNT nanofiller was added to the three-component nanodispersions.

Solid gold/clay/epoxy/MWCNT nanocomposites were prepared from the nanodispersions using an *in situ* polymerization method. A proper amount of amine hardener was added to the respective dispersion at a molar ratio of epoxy resin to hardener of 100:49. The mixture was poured into a cylindrical mold and cured for 24 h at room temperature followed by postcuring at 100 °C for 4 h. The nanocomposites contained 2 wt% organoclay, 0.5 wt% MWCNT, and the gold nanoparticle content varied from 0.04 to 1 wt% AuNPs.

Characterization methods

Transmission electron microscope JEOL JEM 2100 with selected area electron diffraction (SAED) was used for local area characterization of sample morphology and element analysis. Powder samples were deposited on the TEM holders. High magnification TEM has been provided with magnification from 50 to 1 500 000 times.

Microwave measurements were conducted with RS-408R (ELMIKA) analyzer. IEC 62431:2008(E) standard was used to select the method for measuring the reflective properties of electromagnetic materials during normal radiation. The electromagnetic response of the samples represented as a ratio of transmitted through signal (S21) to reflected signal (S11) was measured in the high frequency spectrum from 0.1 to 1 THz. This spectrum is important due to limited number of materials that can provide protection against such radiation. The measurements were conducted at Institute for Nuclear Research, Belarusian State University, Minsk, Belarus as part of FP7 FET Flagship-ICT- 604391 Graphene project.

RESULTS AND DISCUSSION

Figure 1 shows a TEM image of the synthesized gold nanoparticles using wet impregnation method on the surface of organoclay before and after UV treatment of the powder. The size and the shape of the gold nanoparticles shown in the TEM image could be further analyzed using PEBBLES software, namely a user-friendly tool, which implements an accurate, unbiased, reproducible, and fast method to measure morphological parameters of nanoparticle (NP) populations from TEM micrographs [15].

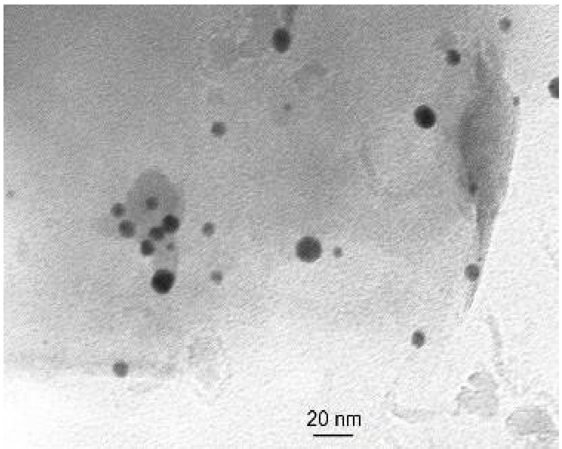

Fig. 1. TEM image with 200 000 times magnification of a sample obtained using wet impregnation method.

Figure 2 shows a TEM image of the sample shown in Fig. 1 using a smaller magnification of 50 000 times. The observed nanoparticles have various shapes, mostly spherical, but also ellipsoid, cylindrical, triangular, or pentagonal.

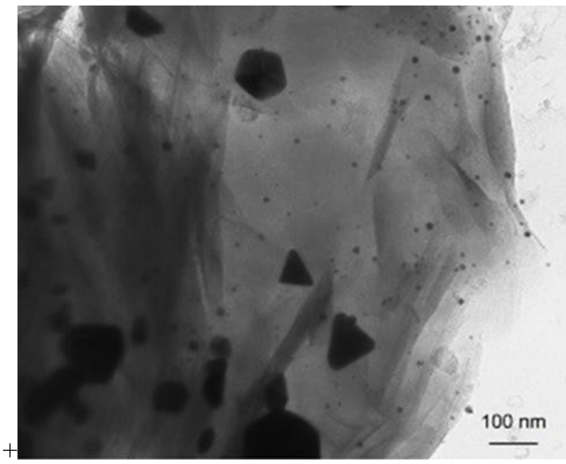

Fig. 2. TEM image with 50 000 times magnification of a sample obtained using wet impregnation method.

Table 1. Statistical analysis of gold nanoparticle size

	Statistical analysis of gold nanoparticle size (nm)				
Method	Mean	Standard Deviation	Minimum	Medium	Maximum
Wet impregnation	35.63	34.31	10.30	16.86	146.69

The agglomeration effect can be attributed to the UV treatment that induces further aggregation of the gold nanoparticles [16]. Results from the statistical analysis of the TEM images are shown in Table 1. To investigate the electromagnetic transmittance of nanocomposites in the high frequency spectrum of 0.1–1 THz, the samples were prepared as thin squares with thickness of 1 mm. Figure 3 shows the electromagnetic transmittance of the nanocomposites for the various frequencies.

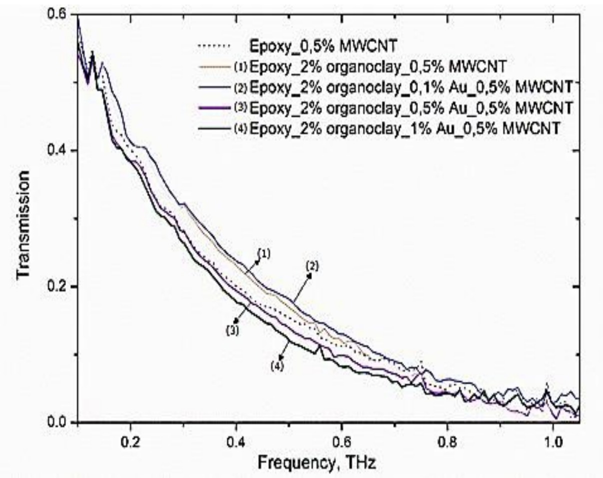

Fig. 3. Electromagnetic properties of epoxy/ organoclay/MWCNT/Au nanocomposites measured in the high frequency spectrum.

Lower transmittance values of 0.1–1 THz were observed in the high frequency zone for a high amount of gold nanoparticles (1 wt.% AuNPs). Inserted gold nanoparticles increased the MWCNT effect and improved the electromagnetic shielding behavior of the nanocomposites.

CONCLUSIONS

In the present study, gold nanoparticles over organoclay were prepared using wet impregnation method with distilled water as solvent. The prepared gold nanoparticles were characterized by TEM. The electromagnetic properties of the nanocomposites were studied by applying a microwave measurement analyzer. Results from the electromagnetic study show that epoxy/ organoclay/gold/ MWCNT nanocomposites with concentration of 0.5 wt% MWCNTs and 1 wt% AuNPs are promising materials for high-frequency electromagnetic wave absorbers.

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