

Microwave Properties of GNP-Polymer Composites with a Segregated Conductive Network

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This work presents the results of investigation of the electrodynamic and shielding characteristics in the range of 40-60 GHz of polymer composites with graphite nanoplatelets and two different types of polymers. Ultra-high molecular weight polyethylene and Nylon 12 polyamide were used as a polymer matrix. It was found that the uniformity of the polymer particle size distribution in a composite strongly affects the value of the percolation threshold of the electrical conductivity of composites, namely, the lower the particle size dispersion, the lower the percolation threshold. The dielectric permittivity dependences on the filler concentration of investigated composites do not have percolation behavior and are almost independent of the electromagnetic radiation (EMR) frequency and the radius of polymer globules. At the same time, the uniformity of the particle size distribution has a positive effect on the increase in the absorption of electromagnetic waves in the material, which is confirmed by higher absorption characteristics in nylon-based composites compared to composites with polyethylene.

Keywords: Segregated structure, Microwave properties, Polymer nanocomposites, Dielectric permittivity.

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1. INTRODUCTION

Composite materials (CMs) consisted of a dielectric polymer and an electrically conductive nanocarbon filler are well known as promising materials for the manufacture of protective electromagnetic shields, chemical sensors, and other applications [1-3]. The reason for this is their unique properties, which provide lightweight, corrosion resistance, mechanical hardening, low cost, and ease of manufacture of such CMs [4, 5]. Particles with a high aspect ratio, as a rule, agglomerate into clusters, which causes rapid degradation of the transport properties of CMs [6, 7]. Creating a conductive network with a high local density of the filler [8] significantly improves the properties of composites [9-11]. Such composites are called segregated (SCMs). The use of SCMs allows to significantly reduce the amount of conductive filler and creates conditions for good absorption of electromagnetic radiation (EMR) by such materials. Polymer composites with the so-called segregated carbon cluster structure can be a good solution for obtaining high shielding characteristics at low bulk (mass) filler content.

The most common method of manufacturing SCMs is thermal packaging (compression) [8]. In the first step, a mechanical mixture of polymer powder and filler with particle sizes D and d , respectively, is formed under the condition $D \gg d$, so that filler particles cover the surface of larger polymer particles, creating a "shell structure". After thermal packaging (compression at the softening temperature of the polymer), the initial distribution of filler particles remains virtually unchanged at the boundaries between polymer grains and forms a pattern of a segregated structure, while poly-

mer particles deform and agglomerate under pressure to form a solid polymer matrix. To obtain the specified electrical properties of SCMs, the processing conditions are important – temperature and compression time, as well as mechanical and rheological properties of the polymer matrix that affect the formation of a segregated structure [12].

SCMs based on graphite nanoplates (GNPs) were studied in [8, 12-14]. It was shown that a segregated structure leads to an increase in thermal stability, elasticity modulus and glass transition temperature of the composite. The magnitude of the shielding efficiency of the composite increases when the concentration of GNPs increases. In a composite of 15 wt. % graphene nanoplates/polymer, the value of the shielding efficiency is ~ 33 dB [15]. At this value, the composite is suitable for widespread use in electronics. At a higher concentration of graphene nanoplates, the value of the shielding efficiency of ~ 83 % was achieved due to absorption losses.

In [16], a composite with a segregated structure based on hybrid filler graphite (Gr)-carbon nanotubes CNTs (Gr-CNTs) and ultra-high molecular weight polyethylene (UHMPE) was obtained. The composite shows excellent electrical conductivity of 195.3 S/m and ultra-high shielding efficiency of electromagnetic radiation of 81.0 dB. These results are higher than for simple graphite or CNTs in a polymer matrix, which confirms the synergistic effect of graphite and CNTs. The aim of this work is to study the influence of the nature of the distribution of conductive filler in a polymer matrix and the type of polymer matrix on the dielectric and electrodynamic properties of composites with GNPs.

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2. MATERIALS AND METHODS

2.1 Materials

As a polymer matrix two types of polymers were used:

– Ultra-high molecular weight polyethylene (UHMWPE) Hostalen GUR (PE), type GHR 8110, supplied by Hoechst AG (Schkopau, Germany) in a powdered form with a particle size of 125/90 μm was used as the polymer matrix of segregated systems. The UHMWPE density was $\rho = 0.93 \text{ g/cm}^3$, its melting temperature was $T_m = 132 \text{ }^\circ\text{C}$.

– Nylon 12 (Nylon 12, polyamide 12) is a polymer with the formula $-(\text{CH}_2)_{11}\text{C}(\text{O})\text{NH}]_n$. Melting point of Nylon 12: 178-180 $^\circ\text{C}$, density: 1.01 g/cm^3 . This Nylon is used as a material for 3D printing by SLS method, so the powder is sieved and has minimum size dispersion.

As a conductive filler we used GNPs. GNPs were obtained by thermo-exfoliation of oxidized natural graphite with following ultrasonication (in Baku 9050 device with a maximum output power of 50 W and an ultrasound frequency of 40 kHz) in acetone medium for 3 h. The peculiarity of the obtaining and morphology of TEG particles are presented in [3].

2.2 Preparation

The samples of segregated polyethylene-based composites with GNPs were prepared by the hot compacting method: in the case of GNP-PE CMs the mechanical mixture of PE and GNPs powder was homogenized by thorough triturating in the porcelain mortar to create the shell layer of carbon filler on the surface of the PE particles. Then the mixture was placed into a hot die (of enclosed type) heated to 160 $^\circ\text{C}$ and pressed (hot compacted) during 5 min at 50 MPa with subsequent cooling down to room temperature [17]. In the case of GNP-Ny composite mixture of Nylon and GNPs in the form of powders were homogenized by thorough mixing using a homogenizer IKA ULTRA TURRAX Tube Drive in a test tube with a stirrer with rotation speed 3000 rpm, during 40 min, then powders were heated to 168 $^\circ\text{C}$ and compacted during 10 min at 110 MPa.

GNP/PE and GNP/Ny SCMs with a filler content of 0.5-5 vol. % of GNPs were prepared in the form of cylinders with a diameter of 30 mm (GNP/PE) and 15 mm (GNP/Ny), and with a height of 1 mm.

Microscopic studies of composite samples were performed by using an optical microscope (“Mikmed-1” with ETREK PCM-510 attachment). Fig. 1 presents optical images of GNP/UHMPE and GNP-Ny SCMs after hot compacting.

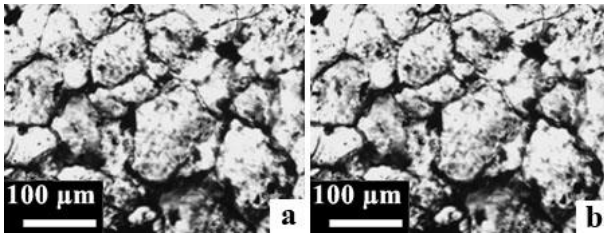


Fig. 1 – Optical images of GNP conductive network formation in SCMs: (a) 1 % GNP/UHMPE; (b) 1.1 % GNP/Ny

As we can see from the figures, the structure of the distribution of GNP conductive particles corresponds to the so-called segregated structure. A smaller dispersion in the size of polymer particles and a more uniform distribution of the carbon component are observed in CMs based on Nylon in comparison with CMs based on polyethylene, where there are larger agglomerates of GNPs and a significant dispersion in particle sizes.

3. ELECTRICAL AND ELECTROMAGNETIC SHIELDING MEASUREMENTS

The DC electrical conductivity σ_{DC} was measured using a two-contact scheme. A sample was held between two steel electrodes and measured under 100 V voltage using E6-13 teraohmmeter Radiotechnika (Riga, Latvia). The values of σ were estimated using the following equation:

$$\sigma = \frac{1}{R} \frac{h}{S}, \quad (1)$$

where R is the electrical resistance measured experimentally, h and S are the sample thickness and area, respectively.

The EMI shielding properties of the composites were tested in a frequency range of 26-37 GHz at room temperature using P2-65 device (the equivalent of a microwave network analyzer), Keysight PNA N5227A vector network analyzer equipped with a rectangular waveguide to coax adapter from 40 to 60 GHz (QWA-19R18M, Quin Star Technology, inc.) to determine the electrodynamic parameters of the investigated composites in EHF-band by the transmission line method. The rectangular waveguides have the following dimensions: 7.2×3.4×3.4 mm^3 and 4.8×2.4×18.2 mm^3 . The shape of the investigated samples provided the overlap of the cross-section of a rectangular waveguide. The thickness of the prepared samples was 1 mm.

Using S -parameters and power balance equation [18, 19], the EMR reflection R , transmission T and absorption A indices were determined:

$$R = |S_{11}|^2, \quad T = |S_{21}|^2, \quad A = 1 - |S_{11}|^2 - |S_{21}|^2. \quad (2)$$

The complex permittivity (ϵ_r) was determined from the scattering parameters using the Nicolson-Ross method.

4. RESULTS AND DISCUSSION

Fig. 2 shows the electrical conductivity of segregated systems GNP/UHMPE, GNP/Ny and with the random distribution of GNP/epoxy filler versus GNP content. As it is seen from Fig. 2, composites demonstrate the percolation behavior and can be described by the following relation [20]:

$$\sigma = \sigma_f (\varphi - \varphi_c)^t \quad \text{at } \varphi > \varphi_c, \quad (3)$$

where t is the critical index, φ_c is the critical concentration or, in other words, the percolation threshold, σ_f and σ_p are the conductivities of the conductive phase and the polymer matrix, respectively.

As expected, GNP-UHMPE and GNP-Ny composites with segregated structures have a much lower value of percolation threshold ($\phi_c \sim 0.95$ vol. % and 0.81 vol. %, respectively) than GNP/epoxy composites with the random distribution of GNP ϕ_c value (~ 2.3 vol. %) and higher values of electrical conductivity.

It is known that in segregated systems, ϕ_c does not depend on the type of polymer matrix but is determined by the ratio of the sizes of the filler and matrix particles, as well as the shape of the filler particles [21]. Namely, the D/d ratio is significant (where D is the size of the polymer particle, and d is the size of the conductive filler particles), the larger this ratio, the lower the percolation threshold.

The size of the PE globules is 95/120 μm , the nylon particles are smaller (about 60 μm), but we see a shift in the percolation threshold in the concentration dependence of the electrical conductivity for nylon-based composites towards lower concentrations. In our previous work [22], we established by numerical simulation that the enhancement of electron transport properties strongly depends on dielectric fraction as well as on the type of spatial distribution of polymer particles. The more ordered polymer network will be created, the better conductivity will be obtained. Randomly distributed polymer particles cause the formation of random filler puddles, which can be excluded from the main conductive network and degrade the properties of the resulting composite. So, the lower size dispersion of nylon particles is the reason why we observe a lower percolation threshold for nylon-based CMs in comparison with UHMPE-based CMs.

Fig. 3 shows the dependences for the real and imaginary parts of the dielectric permittivity. The real part of the dielectric permittivity ϵ' of UHMPE CMs is slightly lower than that of nylon CMs and has a more

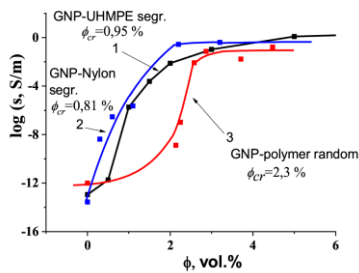


Fig. 2 – Concentration dependence of conductivity for composites with GNPs and different types of polymer network: UHMPE (1), Nylon (2), and epoxy resin (3)

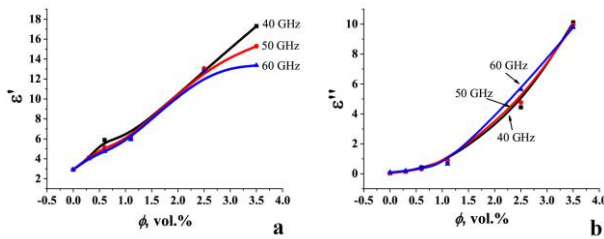


Fig. 3 – Real (a) and imaginary (b) parts of the dielectric permittivity of Ny-based composites filled with GNPs versus filler concentration for different frequencies

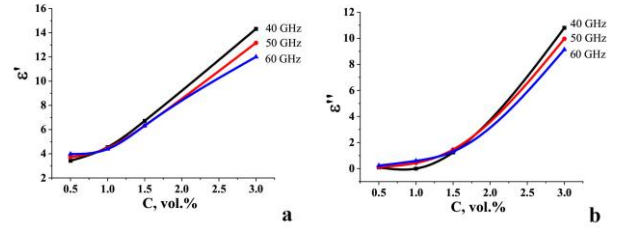


Fig. 4 – Real (a) and imaginary (b) parts of the dielectric permittivity of UHMPE-based composites filled with GNPs versus filler concentration for different frequencies

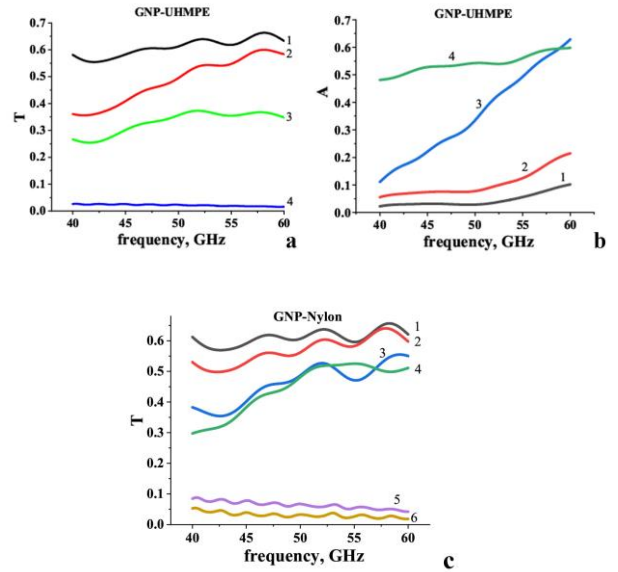


Fig. 5 – Frequency dependences of the transmission T and absorption A coefficients of composites: GNP-UHMPE (a, b) (1 – 0.5 vol. % GNP, 2 – 1 vol. % GNP, 3 – 1.5 vol. % GNP, 4 – 3 vol. % GNP) and GNP-Nylon (c) (1 – 0 vol. % GNP, 2 – 0.3 vol. % GNP, 3 – 0.6 vol. % GNP, 4 – 1.1 vol. % GNP, 5 – 2.5 vol. % GNP, 6 – 3.5 vol. % GNP)

pronounced dependence on frequency. The imaginary parts of the dielectric permittivity ϵ'' at concentrations below the percolation threshold are almost the same in both cases of composites. At a higher concentration of filler ϵ'' of UHMPE-based CM begins to grow faster and at concentrations above 2 vol. % becomes higher than ϵ'' of composites with Ny.

The dielectric permittivity of GNP-Nylon CMs, as well as GNP-UHMPE CMs, does not exhibit percolation behavior, in contrast to electrical conductivity which has a percolation transition at 0.81 and 0.95 vol. %, respectively. It increases monotonically with increasing concentration. The imaginary part of ϵ'' almost does not depend on the frequency, and the real part has a decreasing dependence in both cases at concentrations higher than 3 vol. % GNP.

For the analysis of the EMR absorption efficiency in CMs with segregated fillers distribution, it is convenient to use the reduced absorption index, which is defined as $A_{eff} = A/(1 - R)$. Fig. 6 shows the frequency dependences of the index A_{eff} and changes of A_{eff} versus GNP content for the composites with UHMPE and Ny as polymers.

Fig. 6 shows that the effective absorption coefficient of CM with nylon is higher than that of CM based on PE at concentrations of GNPs lower than the percolation threshold. As the GNP content increases, the A_{eff} values of both types of composites coincide. With a further increase of the concentration of GNP content in CM with UHMPE the absorption will be higher than in CM with nylon. This is due to the higher value of ε'' of GNP-UHMPE CMs and possibly to the larger size of dielectric globules.

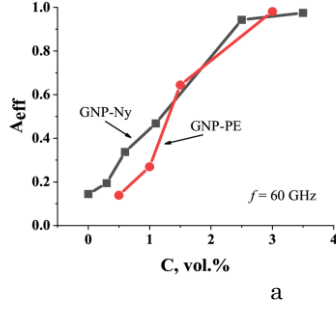


Fig. 6 – GNP content at a frequency of 60 GHz: 1 – 0.6 GNP-Ny, 2 – 1.1 GNP-Ny, 3 – 3.5 GNP-Ny, 4 – 0.5 GNP-PE, 5 – 1 GNP-PE, 6 – 3 GNP-PE

The electromagnetic wave propagates through the medium, the reflectivity is affected by many factors, and not only by permittivity or permeability. It also depends on sample thickness and electromagnetic wave frequency. To investigate the possibility to widen the range of strong absorption and increase the absorbing peak value for the composites with a low concentration of GNPs, we simulated the reflection loss (RL (dB)) by applying the transmission line theory. RL of EMR under normal wave incidence at the surface of a single layer material backed by a perfect conductor can be defined as [23]:

$$R = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|, \quad (4)$$

where $Z_0 = \sqrt{\mu_0/\varepsilon_0}$ is the characteristic impedance of free space, $Z_{in} = \sqrt{\mu_0\mu/\varepsilon_0\varepsilon} (\tanh j2\pi f \sqrt{\mu_0\mu\varepsilon_0\varepsilon} d)$ is the input impedance at the interface of free space and material.

RL has been simulated for GNP/Nylon and GNP/PE composites with different concentrations of filler and different sample thicknesses using experimental data for ε' and ε'' . To compare how the size of polymer granules and the polymer type affect the absorption characteristics of segregated CMs at different sample thicknesses, we calculated RL depending on the frequency and thickness of samples for GNP-UHMPE and GNP-Nylon segregated systems.

The analysis of microwave absorption performance of the investigated composites has shown that composites with the segregated structure of GNPs have high absorption characteristics. In Table 1, one can see that all numerically researched composites have strong wide absorption peaks at the different thicknesses of a sample, in the case of 1.1 vol. % GNP-Ny CM, the effective bandwidth d_f is 7.2 GHz, with $RL_{min} = -31.56$ dB, and in the case of 1.5 vol. % GNP-UHMPE CM, d_f is 7.5 GHz.

Also, it is shown by the simulation results that nylon-based CMs exhibit higher absorption of EM radiation compared to polyethylene-based composites. It can also be seen from Table 1 that at almost equal content of GNPs (1 and 1.1 vol. %) in different polymers broader absorption peaks are observed at smaller sample thicknesses in CMs based on nylon. Even at a higher concentration of GNP in polyethylene (1.5 vol. %) compared to 1.1 vol. % GNP-Ny at the same thicknesses as for GNP-nylon, the depth of the observed peaks is much smaller.

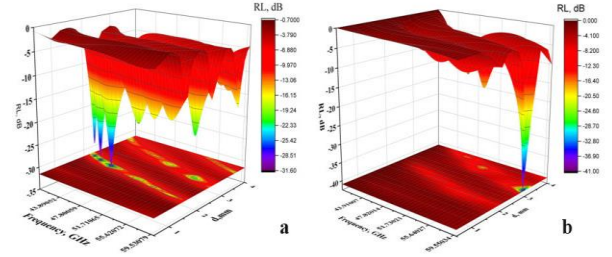


Fig. 7 – The reflection loss versus frequency and thickness for a) 1.1 vol. % GNP-Nylon, b) 1 vol. % GNP-UHMPE

Table 1 – Microwave absorption properties of different GNP-polymer composites

Thickness d , mm	Effective bandwidth d_f , GHz ($RL \leq -10$ dB)	Main absorption peak f_{min} , GHz	RL_{min} , dB
1.1 vol. % GNP-Ny			
1.8	6.5	51.28	-19.4
2	7.2	45.33	-31.56
2.7	5.2	56.7	-22.29
1 vol. % GNP-UHMPE			
3	> 5	59.7	-40.9
3.5	5	50.9	-18.24
3.8	3	46.7	-16.4
1.5 vol. % GNP-UHMPE			
1.8	8	49.87	-11.53
2	7.5	43.73	-17.25
2.7	3.15	55.1	-10.8

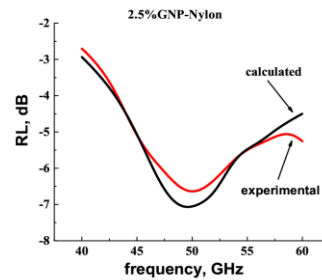


Fig. 8 – Experimental and calculated frequency dependences of reflection loss (RL) of 2.5 vol. % GNP-Nylon CM

To verify the correctness of the calculations, we compared the experimental result of the measurement of RL of 2.5 vol. % GNP-Ny composite, which was studied in the short-circuit mode in the range of 40-60 GHz with the values of RL calculated according to (4), the comparison result is shown in Fig. 8. One can see that the experimental and calculated curves almost coincide which confirms that our calculations are correct.

5. CONCLUSIONS

A series of samples of polymer composites based on GNP and two types of polymers, nylon and UHMPE, with concentrations from 0.5 to 5 vol. % GNP have been manufactured. The concentration dependences of their conductivity, concentration and frequency (40-60 GHz) dependences of the shielding and electrodynamic properties have been studied. It was shown that the homogeneity of the size distribution of polymers has a strong influence on the percolation threshold. It was also shown that the dielectric permittivity dependences on the filler concentration of investigated composites do not exhibit the percolation behavior and is almost independent of the EMR frequency and the radius of the polymer globules.

The absorption of EMR by the investigated composites increases with the increasing filler concentration.

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Мікрохвильові властивості ГНП-полімерних композитів з сегрегованою провідною мережею

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У роботі представлені результати дослідження електродинамічних і екрануючих характеристик в діапазоні 40-60 ГГц полімерних композитів з графітовими нанопластинками і двома різними типами полімеру. Як полімерну матрицю використовували надвисокомолекулярний поліетилен та поліамід Нейлон 12. Встановлено, що однорідність гранулометричного складу полімеру в композиті сильно впливає на величину перколяційного порогу електропровідності композитів, а саме: чим менша дисперсія розмірів частинок, тим нижчий поріг перколяції. Залежності діелектричної проникності від концентрації наповнювача досліджуваних композитів не мають перколяційної поведінки і майже не залежать від частоти ЕМВ та радіуса полімерних глобул. При цьому однорідність гранулометричного складу позитивно впливає на збільшення поглинання електромагнітних хвиль у матеріалі, що підтверджується більш високими характеристиками поглинання у композитів на основі нейлону порівняно з композитами з поліетиленом.

Ключові слова: Сегрегована структура, Мікрохвильові властивості, Полімерні нанокompозити, Діелектрична проникність.