materials proceedings

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Proceeding Paper

Electromagnetic Microwave Absorption Performances of PVC/AC Composites †

Igor P. Matushko [1,*], Yuriy V. Noskov [2], Vladyslav A. Moiseienko [3], Volodymyr Yu. Malyshev [4] and Liudmyla M. Grishchenko [5]

[1] Faculty of Physics, Taras Shevchenko National University of Kyiv, 03022 Kyiv, Ukraine
[2] Kukhar Institute of Bioorganic Chemistry and Petrochemistry NAS of Ukraine, 02094 Kyiv, Ukraine; yuriy.noskov@gmail.com
[3] Independent Research & Development Laboratory "200k Electronics", 01030 Kyiv, Ukraine; vamrpd@gmail.com
[4] Institute of High Technologies, Taras Shevchenko National University of Kyiv, 03022 Kyiv, Ukraine; vladimir.y.malyshev@gmail.com
[5] Faculty of Radiophysics, Electronics and Computer Systems, Taras Shevchenko National University of Kyiv, 03022 Kyiv, Ukraine; liudmyla.grishchenko@gmail.com
* Correspondence: mipigor@gmail.com
† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net/.

Abstract: Films of composite materials PVC/AC were obtained through the use of a method of thermal pressing of powders of polyvinyl chloride (PVC) and activated carbon (AC) at different mass ratios. TGA, TPDIR and TPDMS methods were used to determine the concentration and study the thermal stability of oxygen-containing functional groups of AC. The morphology of AC was studied via the SEM method. When studying the microwave properties of the obtained films of PVC/AC composite materials, it was found that with an increase in the percentage mass of AC, the reflection coefficient of electromagnetic waves from the sample increases, and it appears that this change occurs according to a linear law. It was established that high concentrations of the filler worsen the radio-masking properties of the investigated PVC/AC composite while at the same time improving the absorption of electromagnetic waves by this material.

Keywords: activated carbon; composite materials; polyvinyl chloride; electromagnetic radiation

Citation: Matushko, I.P.; Noskov, Y.V.; Moiseienko, V.A.; Malyshev, V.Y.; Grishchenko, L.M. Electromagnetic Microwave Absorption Performances of PVC/AC Composites. *Mater. Proc.* **2023**, *14*, 15. https://doi.org/10.3390/IOCN2023-14537

Academic Editor: Minas Stylianakis

Published: 5 May 2023

1. Introduction

It is known that carbon nanomaterials have unique properties, which are determined by their surface chemistry and developed porous structures [1–4]. They are widely used as the fillers of composite materials [5], microporous adsorbents [6], catalyst carriers of organic synthesis processes [7] and are also excellent absorbers of electromagnetic radiation [8]. As part of composite materials, they can be used as materials for applications in stealth technologies in the production of protective coatings for the military and for the development of protective coatings or means of individual protection against electromagnetic radiation [9]. At the same time, it is important to use such fillers to create composite materials that are capable of chemical modification; that is, materials on the surface of functional groups with various natures can be introduced. The use of carbon materials (CM) as fillers is convenient as the original materials usually already have a certain number of oxygen-containing groups on the surface layer [10]. In addition, carbon materials, in particular activated carbon, are quite chemically active [11]. Different types of oxygen-containing groups are present on the carbon surface: carboxylic, lactone, anhydride and phenolic [10], which can interact with functional groups of polymer matrices when creating composite materials, which is important for creating new classes of substances with predetermined properties.

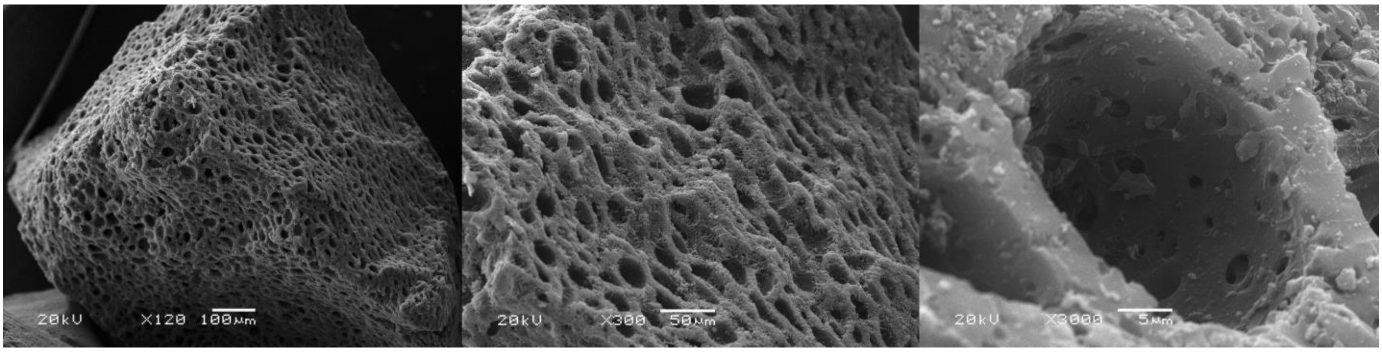
The purpose of this work was to study the influence of chemical modification of AC and its concentration as a filler in the composition of PVC on the interaction of the corresponding PVC/AC composites with electromagnetic radiation in the Ka-band.

2. Materials and Methods

The studies of the AC samples were carried out via thermogravimetric analysis (TGA) using a custom-built thermogravimetric analyzer and thermoprogrammed desorption with the IR registration of the desorption products (TPD IR). Thermal stability was investigated under an argon atmosphere at a flow rate of 50 mL min^{-1} using a heating rate of 10 °C min^{-1} in the temperature range of 30–800 °C. The surface morphology was observed through the use of scanning electron microscopy (SEM) using a Tescan Mira 3 LMU instrument with an acceleration voltage of 10 kV. To study the microwave properties, the microwave reflection (S_{11}) and microwave losses (S_{21}) were measured with a network analyzer (NA) consisting of generator and indicator blocks in the frequency range of Ka-band (26–38 GHz). The dynamic measuring range was 40 dB.

3. Results and Discussion

Activated carbon made from apricot pits, the technology required for the production of which was developed at the Institute of Sorption and Problems of Endoecology of the National Academy of Sciences of Ukraine, with particle sizes of 0.5–1 mm, was used as the starting material. It has a large specific surface and a developed porous structure (Figure 1). The main parameters of the initial samples of AC are as follows: sorption volume of pores by water V_S = 0.41 cm^3/g and a specific surface area of S_{sp} = 1350 m^2/g.



(**a**) (**b**) (**c**)

Figure 1. SEM micrographs of the initial AC with different magnification: (**a**)—120 times, (**b**)—300 times, (**c**)—3000 times.

Using TGA, TPDIR and TPDMS methods, it was established that there are oxygen-containing groups in a small amount on the surface of the original carbon, the desorption of which occurs at different temperature ranges depending on their thermal stability in the form of CO and CO_2 [12]. For the initial AC, a small loss of mass is observed at all temperature intervals, which indicates the presence of a small number of surface oxygen-containing groups (Figure 2). For the sample of the initial AC, there are several maxima of CO_2 release in the temperature range of 250–780 °C; the maxima of CO release correspond to 740 and 900 °C (curve 4). The total release of CO_2 does not exceed 1.2×10^{-4} mol/g and CO—1×10^{-3} mol/g (curve 3).

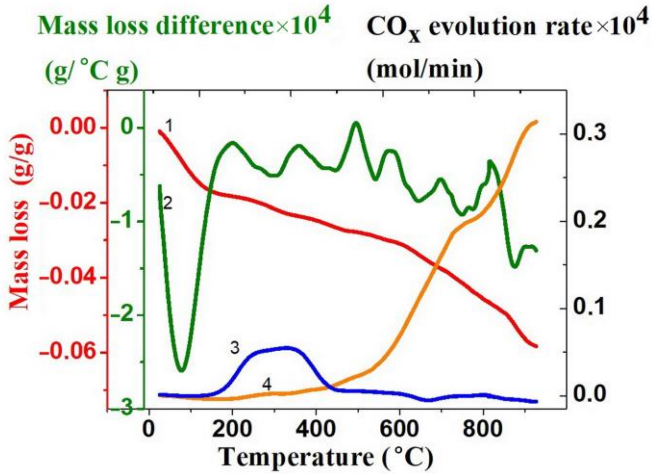
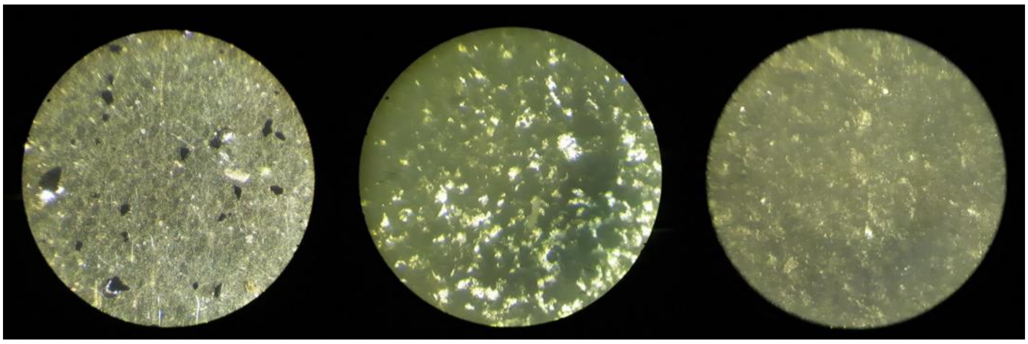


Figure 2. Temperature dependencies of the change in the mass of the initial loss sample in integral (1), differential form (2), CO_2 release rate (3) and CO (4).

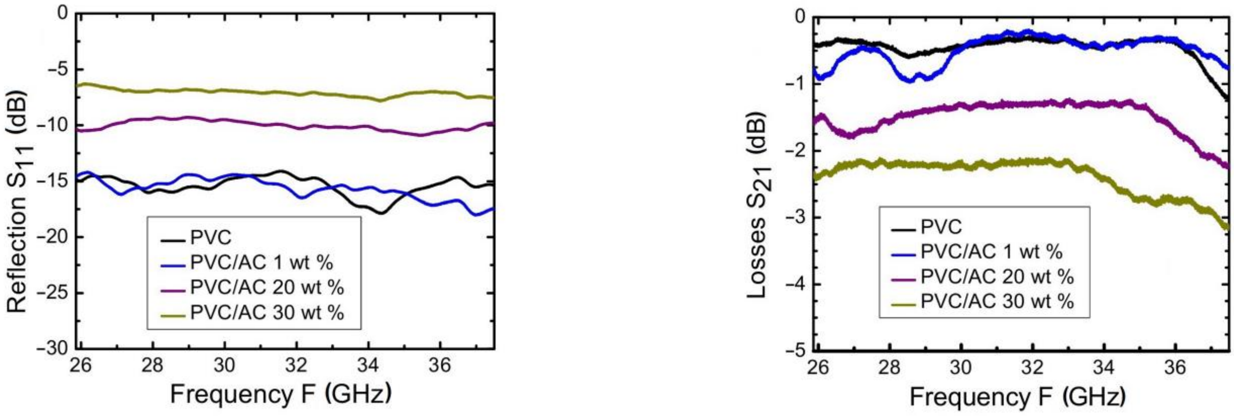
A series of samples of the PVC/AC composite materials were obtained in the form of films via the method of the thermal pressing of polyvinyl chloride (PVC) powders and activated carbon at different mass ratios (1, 20 and 30 wt. % of AC). First, carbon was ground in a mortar. Next, 0.2 g of PVC powder was mixed with the required amount of carbon. This mixture was ground by hand in an agate mortar to a relatively homogeneous state. Then, it was poured into a mold on a polyamide substrate, and 70 mg of dibutyl phthalate (plasticizer for PVC) was dripped. Then, it was pressed at 175 °C under a pressure of 10 MPa with a 1 min holding time. All of the studied samples of pure and modified PVC had a thickness of 0.25 mm. Photos of the obtained composites are shown in Figure 3.



(**a**) (**b**) (**c**)

Figure 3. Photos of the obtained PVC/AC composite materials (composite PVC/AC containing (**a**) 1, (**b**) 20 and (**c**) 30 wt. % of AC, respectively).

Figure 4 shows the results of an experimental study of the ultra-high-frequency properties of pure PVC and PVC/AC composites. The research was carried out using a VNA in the ultra-high-frequency Ka frequency range from 26 to 38 GHz [13]. The coefficient of the S-matrix scattering S_{11} was measured as the reflection coefficient of electromagnetic waves from the surface of the sample under study [14]. From the results shown in Figure 4a, we can see that for pure PVC, the reflection coefficient is -15 ± 1 dB. After adding filler in the amount of 1 wt. %, a change in the reflection coefficient of the material by no more than 10% was obtained.



(**a**) (**b**)

Figure 4. (**a**) Reflection of EM waves S_{11} and (**b**) losses of S_{21} against frequency for PVC/AC composites.

When adding filler in the amount of 20 wt. %, the deterioration of the radio-masking properties of the material was obtained by three times, and after the introduction of all 30 wt. %, the masking properties decreased by 10 times compared to the original PVC sample. At the same time, we note that in the entire frequency range, the value of the reflection coefficient remained constant, and inhomogeneities and "windows of transparency" were not observed. If we continue the analysis of the curves from Figure 4a in the middle of the frequency range, namely at the frequency of 31 GHz, we will obtain a linear dependence of the reflection coefficient S_{11} on the amount of the introduced filler in mass percent, from which it becomes clear that upon reaching the threshold of 55 mass percent, the obtained material will probably start to behave like a metal mirror for electromagnetic waves.

Figure 4b shows the experimental results of the dependencies of the amount of absorption of electromagnetic energy of the samples modified by means of AC and pure PVC in the ultra-high-frequency Ka-band. The coefficient of the S-matrix scattering S_{21} was measured as the coefficient of absorption of electromagnetic waves by the material under study [15]. An absorption value of −0.5 dB was obtained for pure PVC, and the introduction of a modifier in the amount of 1 mass % led to a change in the absorption coefficient of less than 10%, and then only in the lower part of the Ka-band. When adding AC in the amount of 20 and 30% by mass, the values of the absorption coefficient −1.5 dB and −2.2 dB were obtained, respectively.

As with the reflection coefficient, there is a linear change in the amount of absorption of electromagnetic energy by the samples with an increase in the mass percentage of the filler. It is also worth noting the similarities in the properties of PVC after a frequency of 34 GHz; as we can see from Figure 4b, the slope of the curves of the order of 0.5 dB/GHz appears on the frequency dependencies, which indicates a qualitatively different behavior of the material in the next ultra-high-frequency range of waves V-band, which is a remarkable incentive for further research. As already noted above, high concentrations of the modifier worsen the radio-masking properties of the studied PVC/AC material and, at the same time, improve the material's absorption of electromagnetic waves. That is, in the form in which we now see modified PVC, it is ineffective for stealth technology but effective as a protective cover for biological objects.

4. Conclusions

A series of samples of PVC/AC composite materials in the form of films were obtained via the method of the thermal pressing of polyvinyl chloride (PVC) powders and activated carbon at different mass ratios (1, 20 and 30 wt. % of AC). It was found that in the ultra-high-frequency Ka frequency range from 26 to 38 GHz, the coefficient of the S-matrix scattering S_{11} for pure PVC is -15 ± 1 dB, and this value increases with increasing AC content in the sample. The difference in the reflection coefficients between pure PVC and the sample with the highest content (30 wt. % of AC) is 8 ± 0.5 dB. A linear increase in the absorption coefficient S_{21} of electromagnetic energy by the samples with increasing AC content was established. The difference in the absorption coefficients between pure PVC and the sample with the highest content (30 wt. % of AC) is 1.7 ± 0.5 dB. Since the introduction of high concentrations of AC worsens the radio-masking properties of the studied PVC/AC material and, at the same time, improves the absorption of electromagnetic waves by the material, the obtained materials can be useful for protection against the negative impact of biologically harmful electromagnetic radiation on the human body.

Author Contributions: Conceptualization, L.M.G. and I.P.M.; methodology, Y.V.N. and I.P.M.; formal analysis, V.A.M. and V.Y.M.; investigation, V.A.M. and V.Y.M.; writing—original draft preparation, L.M.G. and I.P.M.; writing—review and editing, L.M.G. and I.P.M.; visualization, Y.V.N. and I.P.M. All authors have read and agreed to the published version of the manuscript.

Funding: Grant of the Ministry of Education and Science of Ukraine for perspective development of a scientific direction "Mathematical sciences and natural sciences" at the Taras Shevchenko National University of Kyiv No BF/30-2021, dated 4 August 2021. This work has been supported by Ministry of Education and Science of Ukraine.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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