The effect of reactor geometry on the synthesis of graphene materials in plasma jets

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Abstract. The possibility of synthesis of graphene and graphane (hydrogenated graphene) using the decomposition of hydrocarbons by thermal plasma has been investigated. Investigations of the influence of the plasma-forming gas on the efficiency of synthesis and the morphology of graphene materials were carried out. The synthesis products have been characterized by the methods of scanning microscopy, Raman spectroscopy and thermal analysis. It is found that the morphology of graphene materials is affected by the geometry of the reactor. It was demonstrated that the obtained graphene materials are uniformly distributed in the volume of plastic based on cyanate ester resins under mixing.

1. Introduction
The field of films and coatings continues to develop due to new materials, new methods processing and potential applications. Automobiles, planes, ships, machinery, facades and the interior of buildings, furniture, household appliances, magazines, posters and data storage devices: The list of products covered with lacquers and paints is sheer endless. Surfaces are coated with lacquer or paint to protect them against mechanical, chemical and weather-related impacts but also to improve their aesthetic appearance. To meet the ever-growing demands on modern coatings, the paint industry continuously strives to improve their products. Therefore, over the past years nanotechnology has become more and more important in the development of coatings. Nanomaterials are used to achieve higher opacity, better interaction between coating and surface and higher durability of the coating.

At present, various composites use graphene and hydrogenated graphene (graphane), which is characterized by the presence of hydrogen in its structure. These materials have a number of unique distinctive properties that allow them to be used separately in diametrically opposite areas or together supplement each other [1].

The purpose of this work is to study the possibility of controlled synthesis of graphene and graphane using plasma jets generated by a dc plasma torch and to study the properties of the materials obtained.

2. Methods
To synthesize graphene and graphane, we used a plasma jet reactor, which was previously used for the synthesis of carbon nanotubes. A detailed description of the experimental setup was given in the studies [2]. The experiment involved a simultaneous input of gaseous carbon precursor (methane,
propane-butane mixture, acetylene) with the plasma forming gas (argon, nitrogen, helium) into the plasma torch, wherein heating and decompositions occurred in the plasma jet and in the region of the arc discharge, followed by condensation of the synthesis product on the metal surface of the reaction chamber. The rate of carbon precursor, plasma gas flow and the power of the plasma torch varied independently of each other. For the experimental conditions the electric power of plasma torch was set up to 42 kW. The current value of the plasma torch was constant during the experiment and equaled to 350 A for argon and nitrogen, and 400 A for helium. The flow rate of plasma forming gas varied from 0.75 to 3.0 g/s. The experiment was carried out at three pressure values: 350, 500 and 710 Torr. The hydrocarbon flow rate varied from 0.05 to 0.37 g/s. The time duration of the experiments was 6–10 min. The plasma torch can be attached to two different reactors, without water cooled but one made of stainless-steel and other is made bronze. The first reactor was cylindrical and the second reactor was conical. A cylindrical reactor has 28 cm in diameter and 90 cm in height, and a conical reactor has 100 cm in height and an angle of expansion of 30°. Figure 1 shows the direction of the flow of the vapor-gas stream in the reactor volume.

![Figure 1](image_url)

**Figure 1.** The experimental setup: cylindrical reactor (a), reactor in the form of a cone (b).

To study the synthesis products standard methods to diagnose carbon nanostructures were used. Method of electron microscopy was used to investigate the structure of the synthesized products on a scanning electron microscope of MIRA 3 TESCAN with Schottky field emission cathode in high vacuum regime and scanning electron microscope Hitachi S5500 was used in three modes: SE (displays the surface morphology), BF-STEM (provides a transmission mode), DF-STEM (displays regions that efficiently scatter electrons). Efficiency of the synthesis, thermal stability and phase composition of carbon products were evaluated by thermogravimetry and differential scanning calorimetry on a synchronous thermal analyzer STA 409 PC Luxx (NETZSCH) with linear heating sample in air at the rate of 10 K/min at temperatures up to 1000 °C and in argon at the rate of 5 K/min at temperatures up to 1300 °C. Raman spectra were investigated by using the exciting radiation at a wavelength of 532 nm (Ntegra spectrum). The spectra were taken at three points on the surface of the prepared samples from 100 to 3000 cm⁻¹.

### 3. Results and discussions

Figure 2 presents the typical morphology of graphene materials obtained using the cylindrical reactor geometry. When decomposing hydrocarbons, the products of synthesis are flakes, which are usually observed in the synthesis of graphene by means of thermal plasma [3]. According to the Raman spectroscopy, there are characteristic three peaks on the spectrum. Peak D is observed in the region of 1350 cm⁻¹, peak G is at 1583 cm⁻¹ and the peak of 2D is located at 2680 cm⁻¹. Figure 3 shows the Raman spectrum for a sample synthesized by the decomposition of methane in helium plasma at a pressure of 500 Torr. Analysis of the spectra of graphene flakes obtained by the decomposition of
acetylene showed an increase in the intensity of the D peak, which is explained by increasing the degree of the disorder of the graphene flakes in the sample investigated due to the decrease in their sizes. The use of argon plasma and nitrogen plasma increased the dispersion of the lateral dimensions of graphene flakes. The characteristic size is in the range from 100 to 600 nm at a reactor pressure of 500 or 710 Torr. The effect of pressure changes on morphology was not found.

Using a conical reactor, it was found that the optimal synthesis parameters for the formation of graphene flakes are: pressure in the reactor of 350 and 710 Torr, flow rates of 3.0 g/s for argon, 0.75 g/s for helium and 2.0 g/s for nitrogen. The lateral dimensions of the flakes reach 1.5 μm. On the surface of the synthesized samples, the areas of swelling of the surface are observed. Figure 4 shows this effect. Research of Raman spectra showed that the intensities of peaks D and G are equalized, and for some samples the intensity of peak G decreases. According to [4], these features correspond to hydrogenated graphene (graphane).

Figure 5 shows the characteristic change in mass of the sample of graphane and the desorption rate of hydrogen in the thermogravimetric analysis. The maximum rates of hydrogen evolution are observed at characteristic temperatures [5].

![Figure 2. SEM image of graphene flakes synthesized in helium plasma at 500 Torr. Precursor is methane.](image1)

![Figure 3. Raman spectrum of graphene flakes obtained in helium plasma at 500 Torr. Precursor is methane.](image2)

![Figure 4. SEM image of graphane flakes synthesized in helium plasma at 710 Torr. The precursor is propane-butane.](image3)

![Figure 5. The thermogravimetry of graphane flakes. The precursor is propane-butane. Pressure of argon is 710 Torr.](image4)

Synthesized graphene and graphane were introduced into the cyanate ester prepolymer by simple mixing with heating to 80 °C. Cyanate ester resin (CER) is a modern and promising material with all the properties required for applications in space apparatus engineering [6]. This is thermal stability,
low gas and humidity absorption, high dielectric properties, low outgassing, good resistance to radiation and radio transparency. It is known that the use of carbon nanostructures increases the thermal conductivity of plastics [7]. Studies have been carried out to determine the possibility of embedding graphene materials in a polymer mesh of plastic without affecting its dimensional stability. For this purpose, both graphene and graphene were used. It was found that the graphene, obtained in a conical reactor, is distributed faster and more evenly throughout the volume of the plastic. Figure 6 shows the distribution of carbon nanomaterial in the volume of plastic at two concentrations.

![Figure 6. Microphotographs of cyanate ester resin samples with the addition of graphane: 0.02 mass % (a); 0.05 mass % (b).](image)

4. Conclusion
Graphene and graphene were synthesized during the decomposition of hydrocarbons in a plasma jet reactor. It has been found that the kind of the plasma-forming gas and the type of carbon precursor do not influence the morphology of the synthesis products at pressures of 350 and 710 Torr. It was found that the geometry of the reactor affects the synthesis. When a cylindrical reactor is used, graphene are usually formed, with a conical form, graphane are synthesized. The synthesized samples were flakes with a lateral size of 50 to 1500 nm. The possibility of obtaining graphene materials without the use of catalysts in the reactor volume is shown, which does not require an additional stage of purification from impurities.

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