Synthesis of amorphous carbon nanofibers on a surface of commercial polymers under the action of a high power ion beam of nanosecond duration

V S Kovivchak¹² and Yu G Kryazhev¹
¹Omsk Scientific Center SB RAS, 15 Marx Ave., Omsk, 644024, Russia
²Dostoevsky Omsk State University, 55a Mira Ave., Omsk, 644077, Russia

E-mail: kvs_docent@mail.ru

Abstract. The irradiation of various commercial polymers (chlorinated polyvinyl chloride, polyvinyl chloride, polyvinyl alcohol, polymethyl methacrylate) by a high-power ion beam of nanosecond duration has been investigated. The amorphous carbon nanofibers formation was detected on the surface of low-cost commercial polymers (chlorinated polyvinyl chloride, polyvinyl chloride) containing a catalyst under the high power ion beam irradiation at room temperature. Various iron compounds (organic and inorganic) were used as catalytic additions. The electron microscopy (scanning and transmission) with an energy dispersive analyzer and Raman spectroscopy were used to investigate the morphologies and structure of irradiated polymers. Carbon nanofibers (CNFs) had a most probable diameter in the range 50-90 nm and a maximum length of up to 10 µm. The maximum CNFs growth rate was estimated as 160 µm/µs. A possible growth mechanism for CNFs is discussed.

1. Introduction
Carbon nanomaterials demonstrate promise for a wide variety of applications due to their unique physical and chemical properties. Synthesis of these carbon nanomaterials from low-cost precursors is very important for commercial production. The catalytic pyrolysis of polymer materials can be used to produce carbon nanomaterials. However this process occurs at high temperatures (up to ~1200°C) [1, 2]. This makes it impossible to obtain carbon nanomaterials directly on low-temperature substrates, such as polymers. The formation of a nanostructured carbon layer on the polymer surface can be realized by high-temperature short-time heating of the surface layer of polymer. Pulsed laser radiation, electron and ion beams can be used for such heating. Thus the pulsed laser action on high-temperature polymers (polyimide, phenolic resin) can lead to the formation of carbon layers [3], laser-induced graphene (LIG) [4, 5] and graphene fibers [6] that have a high electrical conductivity.

Other polymers can be used to produce diamond-like films [7], carbon nanosheets [8]. The mechanism of the transformation of various polymers into carbon nanomaterials under laser irradiation is not yet fully understood. The ion and electron beams can also be used to transform polymers into carbon nanomaterials [9–12]. The use of high-power ion beam (HPIB) of nanosecond duration makes it possible to form the nanostructured carbon layer on the surface of inexpensive chlorinated polyvinyl chloride [11]. It should be noted that the establishment of possible growth mechanism for CNFs requires additional research. This is due to the fact that the action of HPIB on polymer materials is
poorly studied. In the article, the features of the formation of nanostructured carbon on the surface of various polymers under HPIB irradiation are considered.

2. Experiments and methods
Polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA) were investigated. These polymers are able to form a carbon-rich solid residue after a high-temperature decomposition. Thin layers (up to 50 µm) of these polymers were deposited onto various substrates from its solution in tetrahydrofuran (for CPVC and PVC, PMMA) or water (for PVA). The solvent were removed by drying at room temperature for 3 days and further at 60°C for 4 h. Organic (ferrocene – Fe(C₅H₅)₂) and inorganic (FeCl₃⋅6H₂O and Fe(NO₃)₃⋅9H₂O) iron compounds were used as catalytic additions. Their content was varied in the range from 1 to 10% of the polymer mass. The "Temp" accelerator (Dostoevsky Omsk State University) was used to irradiate polymers. The parameters of the high-power ion beam used in the work are as follows: ion beam composition of 70% C⁺ and 30% H⁺, ion energy of ~200 keV, current density up to 150 A/cm² and pulse duration of 60 ns. The accelerator chamber has a residual pressure of 5⋅10⁻³ Pa. The morphology and structure of the polymer samples was studied in JSM-6610LV JEOL scanning electron microscopy (SEM) and JEM-2100 JEOL transmission electron microscopy (TEM). The analysis of the elements was carried out with an Inca energy dispersive analyzer built into the microscope. All studied polymers have low surface conductivity. Therefore, a thin platinum layer (~ 10 nm) was deposited on the polymer surface before scanning electron microscopic studies. Room temperature Raman spectra of the polymer samples were recorded on a DXR Smart Raman spectrometer (Thermo Fisher Scientific) using a 632.8 nm wavelength laser.

3. Results and discussion
The initial surfaces of the investigated polymers layers had a close morphology. The typical morphology of such a surface is shown in figure 1a. There are small protrusions which are associated with the non-uniform evaporation of the solvent from the polymer surface layer on the surface. The average transverse dimension of the protrusions in these polymers is ~ 120 nm. HPIB irradiation (with a current density >30 A/cm²) leads to a changes in the polymer surface. During visual monitoring of irradiated polymer surfaces, a significant decrease in surface reflection is usually observed. Since the energy injection duration is negligible (60 ns), the thermal conductivity of the polymers is low (~0.16 W⋅m⁻¹⋅K⁻¹), and the energy release depth is small (~3 µm) then the surface layer temperature will increase appreciably, leading to melting, partial evaporation and decomposition of the surface layer. The irradiation leads to the formation of gas pores with various sizes (figure 1b). In the polymer surface layer open, partially open and closed pores are observed. Pore formation is caused by high internal pressure, which likely arises from the generation of volatile products of polymer decomposition in the region of maximum energy release. Such products are commonly located a small distance from the surface, as was earlier demonstrated for other polymers [13]. Increasing the current density and the number of irradiation pulses leads to an increase in the number of pores in the surface layer. HPIB irradiation of polymers (CPVC, PVC and in some cases PVA) containing iron compounds leads to a significant change in the morphology of the polymer surface.

The arrays of carbon nanofibers (CNFs) are formed on the surface of a CPVC (with a ferrocene additive) after HPIB irradiation with current density of ~100 A/cm² (figure 2a). The nanofibers diameter is 30-200 nm. The maximum fiber length is 10 µm. For this case, we estimated the nanofibers growth rate as 160 µm/µs. TEM analysis showed that the CNFs have an amorphous structure. According to X-ray microanalysis data, nanofibers consist of carbon and oxygen (up to 3%). The irradiated nanofibers were exposed in air.
Therefore oxygen and water vapor were adsorbed on the nanofibers surface. This explains the presence of oxygen in the X-ray microanalysis data. Two broad peaks corresponding to the disordered \(D\) band (1361 cm\(^{-1}\)) and graphitic \(G\) band (1582 cm\(^{-1}\)) appear in the Raman scattering spectrum of irradiated CPVC. Formation of CNFs on the surface of the studied polymers containing water-soluble iron salts (FeCl\(_3\)·6H\(_2\)O or Fe(NO\(_3\))\(_3\)·9H\(_2\)O) at HPIB irradiation has features. In this case, the irradiated polymers have a higher porosity than polymers containing ferrocene. This is due to the removal of water from these hydrated iron salts during their heating upon high power ion irradiation. FeCl\(_3\)·6H\(_2\)O is more preferable catalyst for PVA than Fe(NO\(_3\))\(_3\)·9H\(_2\)O. Most probable CNFs diameter was in the range from 50 to 70 nm for PVA and from 70 to 90 nm for PVC. The nanofiber length does not exceed 2 \(\mu\)m usually. The amount of CNFs formed on the PVA surface was considerably smaller than on the CPVC and PVC surfaces. On the PVA surface the nanofibers are formed only at a current density of \(\sim 70–80\) A/cm\(^2\). The action of an ion beam with the current density of \(> 30\) A/cm\(^2\) on PMMA with iron compounds leads to melting of the surface layer, its partial evaporation and the formation of pores. CNFs do not form. HPIB irradiation causes intense evaporation of the surface PMMA layer due to the depolymerization process (thermal decomposition with the release of the monomer methyl methacrylate), which is characteristic for this polymer. PMMA does not form a carbon-rich residue as a result of thermal decomposition. A high local pressure of gaseous products leads to mechanical fracture of the near-surface layer of the irradiated polymer. The fracture fragments are formed in the region of pores localization.
We assume that the action of high-power ion beam on polymer with catalytic additive results in the decomposition of the polymer and iron compounds and the formation of iron nanoparticles and gaseous products, a solid carbon-rich residue. The iron nanoparticles can be catalysts for the growth of CNFs from gaseous products [11] or carbon-rich residue. The proposed growth mechanism does not explain the high CNFs growth rates. Therefore, the growth mechanism should be studied in more detail.

4. Conclusion
The investigation of the action of a nanosecond high-power ion beam on polymer layers containing iron compound as a catalyst for the growth of carbon nanofibers showed that the formation of carbon nanofibers is observed for chlorinated polyvinyl chloride, polyvinyl chloride and in some cases for polyvinyl alcohol. The observed features of the carbon nanotubes formation on the surface of the investigated polymers under action of the high power ion beam are explained by the difference in the interaction of iron nanoparticles with products of thermal decomposition of the polymers.

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