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Synthesis of Carbon Nanotubes from High-Density Polyethylene Waste

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Abstract

This article presents results of carbon nanotubes synthesis from household high-density polyethylene waste by thermal decomposition. A specific feature of this work is that the decomposition of high-density polyethylene waste and synthesis of carbon nanotubes were carried out in one-step using three-zone chemical vapor deposition reactor. The effect of temperature in the range of 450–550 °C on decomposition products of high-density polyethylene was investigated. The decomposition products of polyethylene wastes were investigated by IR Fourier spectroscopy. Cenospheres obtained from ash and slag waste from thermal power plants during coal combustion were used as a catalyst for the synthesis of carbon nanotubes. The cenospheres were impregnated with an aqueous solution of iron nitrate. It was found that as a result of thermal decomposition of high-density polyethylene waste at temperature of 450 °C, gaseous carbon-containing compounds are formed, which upon further heating to 800 °C lead to the formation of carbon nanotubes with a diameter of 16–21 nm on the surface of catalyst. Physicochemical analysis showed that turbostratic carbon is almost completely absent in the formed product. Carbon nanotubes analysis was performed by scanning electron microscopy and Raman spectroscopy.

1. Introduction

High density polyethylene is a polymer obtained by the low-pressure ethylene-polymerization reaction. High-density polyethylene (HDPE) is intended for manufacture of technical products, as well as products contacting with food, drinking water, cosmetics and medicine, furthermore it is approved for manufacturing toys. Due to the wide range of applications, a large amount of HDPE waste is produced daily. In 2016–2017, about 2.5 million tons of plastic waste was generated [1].

Active research is currently underway on the disposal of high density polyethylene waste. In [2], authors represent results of their studies on the pyrolysis of HDPE in an autoclave under the temperatures from 470 to 495 °C in order to produce liquid combustible fuel. In [3], authors revealed that the pyrolysis of HDPE waste at a temperature of 350 °C leads to the formation of liquid fuels with a high content of olefins and naphthenes, which suits the criteria for the quality of fuels. Gaseous products releasing during the pyrolysis of polyethylene are also essential. Therefore, authors of [4] demonstrate that the gaseous product resulting from the pyrolysis of polyethylene water containers (HDPE) consists of 2.53% ethane, 21.67% propane and 75.82% propylene.

In [5], the authors performed a chromatographic analysis of the decomposition products of HDPE waste at a temperature of 560 °C. It was presented that the main decomposition products of HDPE waste are ethylene, propylene, isobutene, 1-hexene and heptane. Additionally, gaseous products of polyethylene waste decomposition, as shown in [6], mainly contain methane in a temperature range from 250 to 750 °C. However, the methane content in the exhaust gas is highly dependent on the heating rate.

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In [7] authors show the results of studies on the pyrolysis of HDPE, low density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) at a temperature range 550–1050 °C in H_2, N_2, and Ar atmospheres to produce carbon nanomaterials (CNMs). It was shown that HDPE allows to achieve the maximum yield at 750 °C in H_2 atmosphere with a synthesis time of 2 h, resulting in formation of carbon nanobeads and some CNTs. At 1050 °C, more multi-walled carbon nanotubes (CNTs) with a certain amount of carbon nanobeads were obtained.

In [8], the authors demonstrate remarkable results in the synthesis of carbon nanotubes from plastic waste in a stainless steel reactor with the best results shown by CNT samples obtained at a temperature of 900 °C. Possibility of synthesis of carbon nanotubes by catalytic pyrolysis of plastic waste on a nickel – stainless-steel mesh at temperatures of 700–900 °C was presented in [9]; it was determined that the optimum temperature for the maximum yield of CNTs is 800 °C, which allows to form 334 mg of multi-walled carbon nanotubes (MWNTs) for every 1 g of plastic. In the process of synthesis of carbon nanomaterials, the structure, yield and properties of the final product are influenced by the starting materials, the catalyst [10], but also the synthesis parameters: temperature, time, pressure, etc. [11].

Carbon nanotubes have the prospect of practical application in many industries, including electric power systems, textile industry [12], composite materials for various applications [13], etc.

The aim of this work is to develop a method for producing carbon nanotubes by processing household waste from HDPE. This processing method will allow you to dispose of waste to obtain an economically viable product.

2. Experimental part

Household polyethylene waste presented as containers from food products and cosmetics with the «HDPE» marking, were pre-crushed and subjected to cleaning. Cleaning was carried out by washing the ground sample with hot water with the addition of surfactants with their further removal by repeated washing with running water. Afterwards the samples were dried under normal conditions until removal of moisture.

To study the decomposition and synthesis processes, a three-zone furnace with a quartz tube reactor was installed. The inner diameter of the tube was 6 cm and the length was 120.7 cm. The process of decomposition of high-density polyethylene waste in the temperature range from 450 to 550 °C was investigated. The gas-phase and vapour-phase decomposition products of HDPE were collected at the outlet of the tubular reactor. Precipitation of the products was carried out with laboratory cellulose filters (specific gravity 80 g/m^2, pore size ~ 2–3 μm). Afterwards, decomposition products of HDPE were investigated by IR-spectroscopy using IR Fourier spectrometer Spectrum 65.

During the experiments, preparation of catalyst for CNT synthesis was provided by impregnation of 10 g of cenospheres with an aqueous solution of iron nitrate nonahydrate with a concentration of 100 g/l. Further, the catalyst samples were dried at a temperature of 70 °C for 2–3 h, until the moisture was completely removed.

The decomposition of polyethylene and the synthesis of CNTs were carried out in one stage in a three-zone chemical vapor deposition (CVD) reactor, for this, a quartz cuvette with a 4 g HDPE sample was installed in the first zone of the reactor (temperature 450 °C), a quartz cuvette with a catalyst weighing 1 g was installed in the third zone of the furnace. The temperatures in the second and third zones were set at 700 and 800 °C, respectively. Nitrogen with a purity of 99.9% was used as a transport gas with a flow rate of 530–540 cm^3/min. Synthesis lasted 30 min. Samples of carbon nanotubes were studied by scanning microscopy (Quanta 200i 3D B JEOL, JSM-6490LA) and Raman spectroscopy (NT-MDT NTegra Spectra), which allowed us to evaluate the morphology and structure of the obtained CNTs.

3. Results and discussion

It was experimentally established that, at temperatures below 400 °C, thermal destruction of polyethylene waste does not occur to a sufficient degree; only slight sintering of the samples is observed. Thermal decomposition of polyethylene waste occurs with release of white smoke with a specific odor. The composition and quality of volatile products are defined by chemical and physical properties of polymer and conditions of a process. The size of molecular fragments must be small enough to be volatile at the decomposition temperature. This effectively defines the upper limit of molecular weight of the volatiles. If larger fragments of a chain are created, they will remain in a condensed phase and will subsequently decompose into smaller fragments that can evaporate [14].

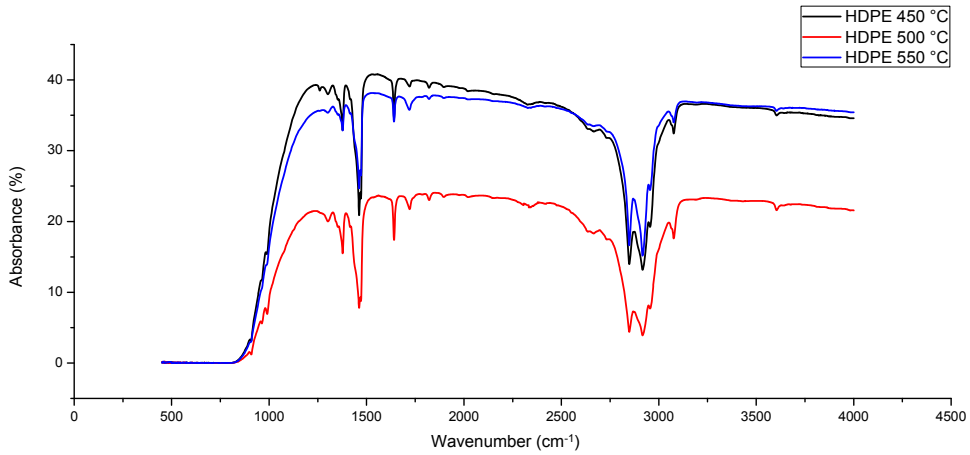


Fig. 1. IR-spectra of the decomposition products of HDPE at various temperatures: black – 450 °C; red – 500 °C; blue – 550 °C.

The kinetics describing the decomposition of polyethylene can be quite complex. The most common assumption is that reactions can be described by a first-order Arrhenius expression.

To identify the structure of the decomposition products of high density polyethylene, the method of infrared spectroscopy was carried out. Figure 1 shows the IR-spectra of products at temperatures of 450, 500, and 550 °C respectively.

Comparing the spectra presented for the products of HDPE decomposition at different temperatures, it can be observed that, basically, all peaks are most well-defined for the pyrolysis products at 450 °C, and their intensity usually tends to decrease with increasing temperature.

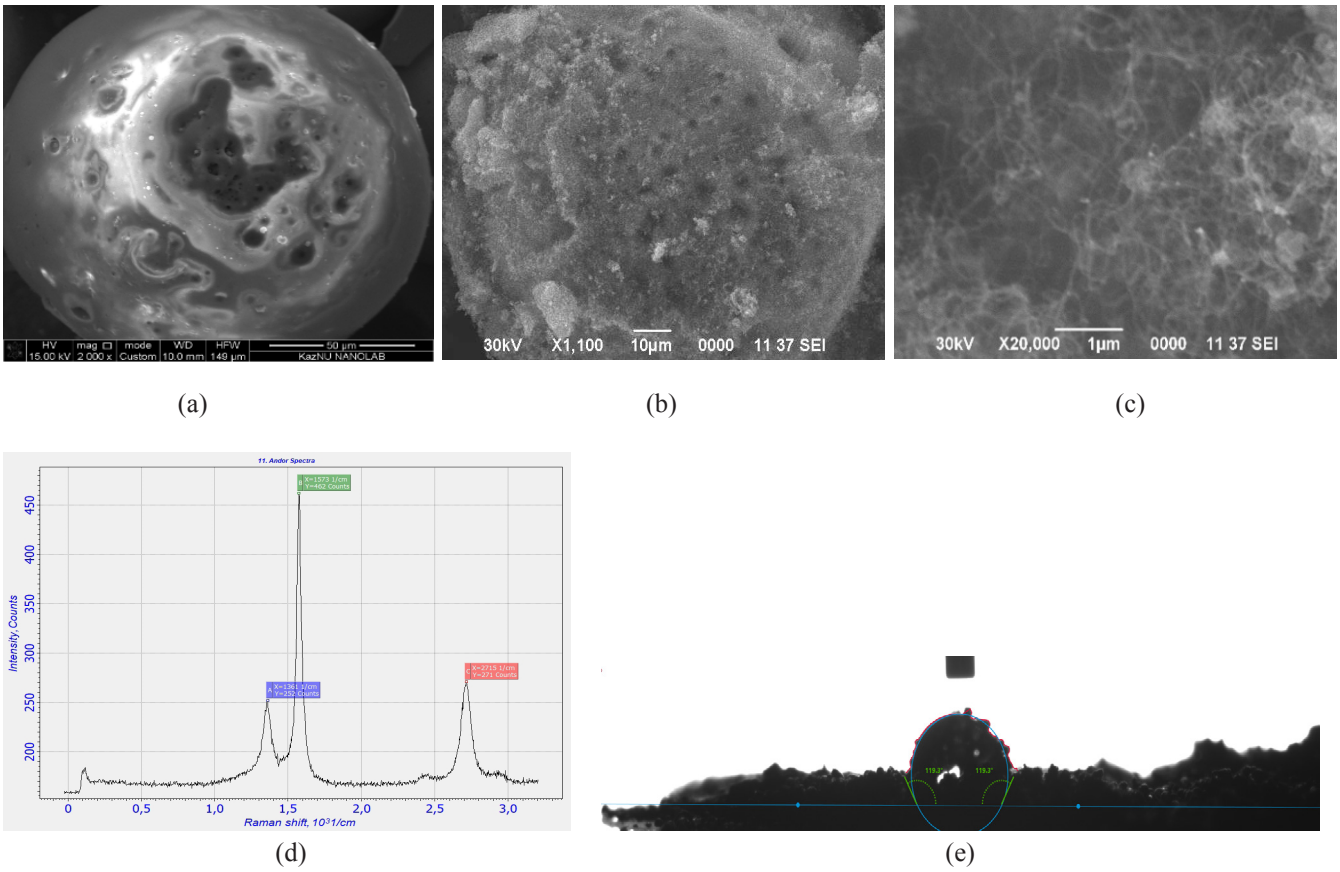
A weak peak at a frequency of 3076 cm^{-1}, corresponding to tensile vibrations of C–H bonds in aromatic compounds, has a poorly structured morphology in all three cases, and its intensity decreases with increasing temperature. The peaks corresponding to a frequency of 1641 cm^{-1} characterize a double C–C bond (both carbons in sp^2 hybridization). With an increase in temperature from 450 to 500 °C, intensity of this peak remains almost unchanged, whilst a slight decrease occurs upon heating to 550 °C. This peak may indicate presence of alkenes.

All three spectra show a well-structured adsorption peak at 1462 cm^{-1} which indicate presence of CH_2 groups, this peak gradually decreases with increasing temperature. Also a group of peaks with nonlinear fluctuation in severity was observed. Furthermore, in all three spectra there are peaks in the range of 2915–2940 cm^{-1}, which correspond to aliphatic C-H-bonds and vibrations at a frequency of 2849 cm^{-1}, which correspond to symmetric methyl groups. These peaks reflect presence of alkanes in the samples. Interestingly, in the temperature transition from 450 to 500 °C, presence of these peaks in spectra decreases, i.e. in this temperature range, a reaction with a participation of saturated compounds is possible. With a further increase in temperature, number of alkanes increases again.

Thus, the processing of high density polyethylene at 450–500 °C leads to a more noticeable presence of unsaturated compounds in the pyrolysis products. An increase in temperature to 550 °C during the pyrolysis of polyethylene in an inert atmosphere promotes an increase in alkanes formation.

As can be seen from the results of IR-spectroscopy, the decomposition products of HDPE in a temperature range 450–550 °C do not vary in terms of composition, therefore, a synthesis of carbon nanotubes was carried out at 450 °C.

For the synthesis of carbon nanotubes, cenospheres were used as a catalyst $P'_{100/500}$ (P' – factory marking of cenospheres, 100/500 – sizes of cenospheres from 100 to 500 μm), consisting mainly of silicon and aluminum oxides. The cenospheres were impregnated with a solution of iron nitrate, having the role of a precursor for the formation of iron nanoparticles, which are CNT growth centers. During the synthesis, iron nitrate decomposes to form metallic iron nanoparticles on the surface of the cenospheres (Fig. 2a), which are the active centers of nanotube growth. Figure 2b, c reflects SEM images at various magnifications obtained for carbon nanotubes synthesized on a $Fe@P'_{100/500}$ catalyst from high density polyethylene at a decomposition temperature of 450 °C.



(a) (b) (c)

(d) (e)

Fig. 2. (a) – SEM image of the surface of cenosphere before the synthesis of CNTs; (b) – SEM image of the surface of cenosphere after synthesis of CNTs; (c) – CNTs synthesized on a Fe@P'$_{100/500}$ catalyst from HDPE at polyethylene decomposition temperature of 450 °C; (d) – Raman spectrum of CNTs; (e) – snapshot of a drop of water on the surface of cenospheres coated with carbon nanotubes.

As could be seen from the images in the process of synthesis, a coating of CNTs is formed on the surface of cenospheres. Analysis of SEM images of samples obtained from high-density polyethylene at a decomposition temperature of 450 °C on a Fe@P'$_{100/500}$ catalyst displays that synthesis conduces to formation of high-quality carbon nanotubes, whilst amorphous (turbostratic) carbon is almost absent. Nanotubes have a diameter range of 16 to 21 nm. The Raman spectrum (Fig. 2d) has 3 most pronounced peaks in the region of 1361 cm^{-1} (D-peak), 1573 cm^{-1} (G-peak) and 2715 cm^{-1} (2G-peak), which are in the regions characteristic for MWCNTs. The ratio of intensities I_D/I_G = 0.55 shows a high degree of graphitization and low defectiveness of the obtained CNTs.

Figure 2e illustrates a snapshot of the hydrophobicity analysis for synthesized CNTs using DSA25 equipment for measuring the contact angle. An analysis of wettability of cenospheres covered with CNTs shows that nanotubes impart hydrophobic properties to cenosphere surface. Carbon nanotubes synthesized from HDPE demonstrated good hydrophobic properties; the contact angle of water drop with obtained nanotubes is 119.3 °. This material based on cenospheres coated with carbon nanotubes does not lose its hydrophobic properties even after ultrasonic exposure for an hour. The hydrophobic properties of CNTs do not alter even after prolonged contact with water; it has been established that after 170 h (more than 7 days) the hydrophobic properties remain the same. The hydrophobic properties of the obtained carbon nanotubes are due to the nanoscale parameters of the tubes, which, similar to the "lotus effect" give the hydrophobic properties of the material.

4. Conclusion

Based on the results, authors proposed a method for the synthesis of carbon nanotubes from high-density polyethylene waste. It was experimentally established that the optimal conditions for the synthesis of carbon nanotubes from HDPE waste are met by the followings: catalyst Fe@P'$_{100/500}$ (cenospheres with $Fe(NO_3)_2 \cdot 9H_2O$), temperature

of CNT synthesis is 800 °C, decomposition temperature of polyethylene is 450 °C, nitrogen consumption is 530–540 cm^3/min and synthesis time is 30 min. During the synthesis, carbon nanotubes were obtained, amorphous (turbostratic) carbon was completely absent, and diameter of carbon nanotubes was 16–21 nm. A small variation in diameter indicates the high quality of the obtained carbon nanotubes.

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