CNTs-modified polyethylene/paraffin composite for electric heaters

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Abstract. The present paper describes paraffin/polyethylene-based composites modified with functionalized carbon nanotubes with the ratio ‘length : diameter’ of ‘10:1…100:1’. These composites possess electrical conductivity and are capable of generating heat under direct current supply conditions. The experiments performed showed that under the action of electric current, the composites are heated up to the stable temperature of 48.3 °C. The effect of maintaining such a temperature is associated with the availability of paraffin in the material composition.

1 Introduction

Development of nanostructured composites is within top global technological, research, and economic trends in fundamental and applied research [1,2] Paraffin and polyethylene mixtures modified with carbon nanotubes (CNTs) can be effectively used as heat-accumulating materials attracting the particular attention of an international scientific and technical cooperation.

Functionalized CNTs have the ability to integrate into the polyethylene matrix and ensure the heat-accumulating effect of the materials obtained, providing cost savings and determining the feasibility of introducing this innovation.

Due to high pliability of polymers to modification there have been developed different composites which are resistant to both mechanical stress [3] and erosive wear [4]. Moreover modified polymers possess high electrical conductivity upon reaching the percolation threshold when adding carbon nanomaterials [5,6]. As for carbon nanomaterials, they are very promising fillers for efficient elastification of heat-resistant binders, since they allow simultaneously increasing the deformation characteristics and the elastic modulus of the polymer matrix [7].

Agglomeration of CNTs in a polymer requires the use of methods to improve their distribution [8]. Covalent and non-covalent functionalization, due to which the efficiency of applying nanomaterials significantly increases and their consumption rates decrease [9], is one of the ways to enhance the affinity of carbon nanostructures for modifiable matrices. Carbon nanostructures, capable of significantly improving the physical and mechanical characteristics (bending strength, compression, thermal conductivity, and electrical conductivity) of obtained composites, have recently been used to modify various polymers. To ensure maximum alignment of carbon nanomaterials (CNMs) with the polymer matrix (ABS plastic, polyethylene, or fluoropolymer), it is required that the modifier possess specified characteristics (diameter, length, degree of defectiveness, specific surface area, availability of functional groups, etc). The diameter of the nanostructure being formed depends on the size of catalyst active sites, whereas the length, the amorphous carbon content and the specific product yield depend on the composition of the catalytic system. Therefore, it is important to be able to obtain an effective catalyst, and knowing the features of implementation of the process of its preparation enables the synthesis of nanomodifiers having the characteristics required for the polymers under consideration. The present method of introducing the synthesized nanomodifier into the polymer matrix will make it possible to yield a competitive composite possessing improved characteristics. The paper [10] describes a self-regulating heater manufactured based on a resistive carbon paste. The authors note that the advantages of the designed heater include self-regulation capacity, low supply voltage and temperatures in the range of 30…60 °C.

The scientific significance of the work is connected with the obtaining of new materials with controlled functional properties. Considering the aforementioned, the objective of the present research was to study heat dissipation in a paraffin- and polyethylene-based polymer composite modified with CNTs under the action of electrical voltage.

2 Materials and methods

To obtain CNTs we used nickel-magnesia catalyst with ‘9:1’ weight ratio of ‘Ni:MgO’. . . CNTs were obtained through the chemical vapour deposition on the catalyst using a propane-butane mixture (in a ratio inherent to
natural gas) as a source of hydrocarbons. Pure CNTs were then functionalized with ozonation via gas-phase technology with an ozone-oxygen mixture for 5 h at 20°C.

In our work we had a mixture of low-density polyethylene (Kazanorgsintez, Kazan, Russia) and P-2 paraffin (Lukoil, Moscow, Russia). The weight ratio of paraffin and polyethylene in the mixture was 2:1. Fine-grained polyethylene granules were added to paraffin, and heated to 100 °C under slow mixing prior to adding of functionalized CNTs. The samples of the polyethylene/paraffin composite (PPC) were molded (length x width= 4 x 6 cm) with aluminum current-carrying electrodes. A supply voltage of 24 V was applied to the electrodes. In final CNTs-modified polyethylene/paraffin composite (PPC) we examined thermal and electrophysical properties.

Temperature field distribution on the composites surface was measured by a non-contact temperature method using a Testo 875 thermal imager equipped with a built-in digital camera (Lenzkirch, Germany; detector and lens dimensions: 160 x 120 and 32 x 23 pixels, respectively, temperature range: -20...+350 °C). The degree of blackness of the composite was preliminarily determined using a THK-1087 chromel-copel thermocouple (NGO "Thermoprylad", Lviv, Ukraine) and a Fluke 576 pyrometer (Everett, WA, USA). In order to eliminate the reflection of infrared rays in the direction non-perpendicular to the viewfinder of the thermal imager, and to prevent superposition of the rays, the nanomaterial surface was levelled by overlaying a flat and smooth surface followed by heating and tight pressing. In addition to the measures presented, to eliminate the effect of the infrared ray reflection from the nanomaterial surface, the thermal imager was directed at different angles. The measurements were repeated at least five times. The data on the temperature field distribution were recorded in the memory of the thermal imager, and processed using the TestoIRSoft 3.6 specialized software.

The distribution of equipotential lines on the nanomaterial surface was studied using an Aktakom 1097 multimeter probe (Lutron Electronic Enterprise Co., Taipei, Taiwan).

Morphology of CNTs was examined by a scanning electron microscope Hitachi H-800 (SEM, Hitachi, Japan)).

3 Results and discussion

According to SEM analysis, CNTs have a length of several micrometres (from 89 nm to 120 µm) and diameter of 10...80 nm (Fig. 1). The ratio “length: diameter” is from 10:1 to 100:1.

Paraffin-covered CNTs are evenly distributed during further mixing with the polyethylene. When the CNTs are introduced into the PPC coating, the formation of large agglomerates [8] have observed (Fig.1).

After mixing the CNTs with the paraffin at heating, a uniform layer of the paraffin with the thickness of 5 nm (Fig. 2).

Fig 1. SEM image of the CNTs.

Fig 2. TEM image of the CNTs with a modifying layer of paraffin.

Fig. 3. Distribution of the equipotential field on the surface of the CNTs-modified PPC for end and side arrangements of the supply electrodes.

Fig. 3 shows the distribution of the equipotential field on the surface of CNTs-modified PPC for end and side arrangements of the supply electrodes, whereas Fig. 4 presents the temperature field distribution for the distance between the electrodes equal to 2 cm.
From Fig. 3 it follows that the potential field acquires the greatest value in the central zone and decreases towards the end and side surfaces.

As can be seen from the Fig. 4, the temperature difference is 10 °C, and the maximum temperature in reaches 48.3 °C, thereby achieving temperature self-regulation. The stabilization at this temperature level is associated with phase transitions in the paraffin which softens and changes its volume, leading to an increase in the nanomaterials resistivity. The initial non-uniformity of the temperature field is associated with the non-uniformity of the equipotential lines. After having reached a certain temperature range, the nanomaterial gains thermal energy in accordance with the paraffin thermal capacity in the phase transition mode.

**Fig. 4.** Distribution of the temperature field on the surface of CNTs-modified PPC.

The uniform distribution of the temperature field is associated with the location of the electrodes. By placing the electrodes closer to each other (1.5 cm), you can get a uniform temperature field, but with a lower temperature at 45 °C (Fig. 5).

**Fig. 5.** Distribution of the temperature field on CNTs-modified PPC.

Designed heating elements can be used for heating electrochemical sensors, as well as functional elements for thermal fans and floor and ceiling heaters in rooms.

### 4 Conclusion

We have shown the possibility of employing CNTs-modified polyethylene/paraffin composite in electrical engineering, heat engineering, in heating systems of residential buildings PPC. Thermal energy can be accumulated when electrical energy is converted into thermal energy at the temperature of 48.3 °C, the latter can be accumulated both in the central zone of the nanomaterial, and along its ends. This is due to the arrangement of the electrodes. After mixing the CNTs with the polyethylene followed by heating, a uniform polyethylene layer, having a special structure, was formed on the CNT surface. This interaction feature can be considered as a special case of functionalization.

The development presented herein can be successfully implemented in many areas of heavy industry and engineering.

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