DOI: 10.17277/amt.2016.04.pp.071-076

Experimental Determination of the Thermophysical Properties of Polygraphene-Based Pastes

A.G. Divin, S.V. Ponomarev, D.A. Liubimova*

Department of Quality Management and Certification, Tambov State Technical University,
116, Sovetskaya St., Tambov, 392000, Russia

* Corresponding author. Tel.: + 7 953 706 52 03. *E-mail*: divinadar@yandex.ru

Abstract

Nowadays, graphene-based composite materials are the most promising materials due to their unique mechanical, electrical, and thermophysical properties. The paper presents information on the measurement method and the results of the experimental determination of temperature dependence of heat capacity and thermal conductivity of polygraphene pastes. The well-proven method of monotonous heating was used to determine these dependencies with the help of IT-c-400 and IT-λ-400 devices. The authors modernized these devices by using National Instruments hardware and software. The article presents the functional diagrams of control systems and data underlying the upgraded appliances, as well as the experimental dependences of heat capacity and thermal conductivity on the temperature of polygraphene-based pastes with different composition.

Keywords:

Accuracy; carbon nanoparticles; composite polymers; heat capacity; measurements; polygraphene; thermophysical properties.

Introduction

Increasing product market competition for engineering, construction, aviation and space technology forces manufacturers to develop new materials with improved operational characteristics, such as overstrength, hardness, chemical and heat resistance, etc. The most promising trend in this area is using carbon nanomaterials and composite polymers containing additives of these materials.

Recently, the attention of the researches all over the world has been concentrated on such a modification of carbon as graphene. This is a two-dimensional allotropic carbon modification, formed by a layer of carbon atoms with a thickness of one atom. According to the researchers, graphene has unique strength and thermal conductivity. The technology which has been developed at Tambov State Technical University for producing oxidized multilayer graphene is based on the separation of graphite layers by using chemical oxidants. The oxidation of the inner layers of graphite results from the graphite exposure to strong oxidants. This process is accompanied by an increase in the interlayer distance in a crystal and a decrease in the interaction energy between the layers. The material obtained is dispersed by ultrasound on graphene nanoplates in a solution and then filtered. After the filtration, the paste contains about 7–8 % of a solid substance [1, 2].

Heat capacity is one of the most important properties of any material, including graphene-based composites. This paper is aimed at providing information on the methods and a measurement tool and also the results of measuring heat capacity of graphene-based paste with water and glycerol.

The Experimental Setup

The experimental (measuring) setup for the determination of the polygraphene specific heat capacity dependence on temperature [1] includes a well-established IT-c-400 device, as well as computer-

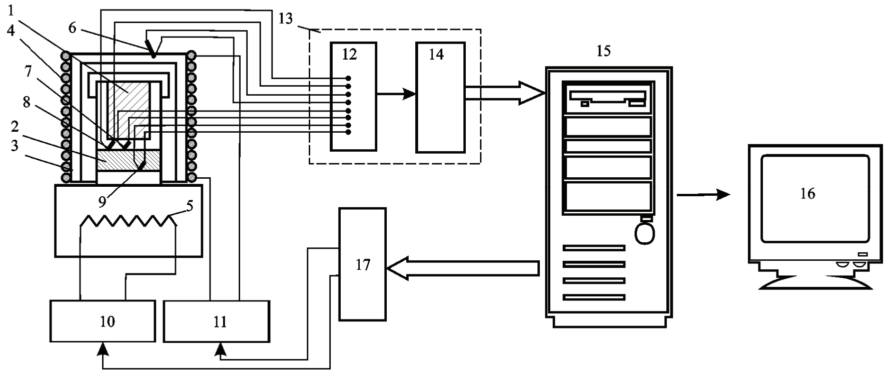


Fig. 1. The functional scheme of the modernized IT-c-400 heat capacity measuring device

aided means for measurements by the National Instruments company [3–6]. The measuring setup realizes the method of monotonous heating, which allows to determine the heat capacity of solid, liquid and bulk materials in a wide temperature range from –100 to +400 °C.

The construction of the measurement setup contains the following units (Fig. 1). The heat flow from heater *5* goes through heat meter *2* into the ampoule with sample *1*. To prevent the heat exchange of sample *1* with the environment, adiabatic cover *3* with heater *4* is used. The temperatures on the upper and lower surfaces of heat meter *2* are registered during the measurement process. The temperature sensors are chromel-alumel thermocouples *7* and *9*, with a nominal static characteristic K.

The voltage from the amplifier is applied to heater *5* and is varied over time so that the temperature on the upper surface of the heat meter and sample temperature depend on time linearly. Therefore, the heating rate during heating process is the constant value. Software control of sample temperature makes it possible to eliminate measurement errors, associated with regulation errors, which were described in [3]. The temperatures of the adiabatic cover and ampoule with the sample are measured by using thermocouples *6* and *8* respectively and kept equal due to the power control of electric heater *4* in accordance with the proportional integral law. The specific heat capacity of the sample is determined indirectly by measuring the delay time of the temperature on the upper surface of the heat meter and the temperature of its lower surface, the sample weight and the constants of the measurement device. Temperature control, experimental data registration and processing are carried out by using personal computer *15* connected with a multifunction data acquisition board PCI-6251 by the National Instruments company. Thermocouples are connected to data acquisition board *13* (NI USB 9211A), which consists of connector *12* and NI USB 9211 block with an amplifier, filter and 24-bit ADC. The board has compensation of thermocouple cold junction temperature and allows performing autocalibration. The use of this board allowed us to significantly increase the accuracy of temperature measurement. This fact has a positive impact on the accuracy of the heat capacity measurement. The adiabatic cover temperature control is carried out according to the adiabatic shell proportional-integral (**PI**) control law, which is implemented in the software. Heating rate of the sample is kept constant by supplying a linearly increasing voltage to power amplifier *5*.

Heaters *4* and *5* are controlled by analog outputs of data acquisition board via power amplifiers *10* and *11*. Effect level is calculated in accordance with the values of the temperature on the lower surface of heat meter *2*, and the temperature difference between the ampoule (with sample *1*) and adiabatic cover *3*.

The automation of measurements allowed us to increase significantly the functionality of the devices. So, it became possible to measure the heat capacity of the materials (by means of modernized IT-c-400 meter) at much lower heating rate (up to 0,025 K/s). This made it possible to observe the laws of phase transitions of polymer materials, to determine the temperature and enthalpy of melting.

The heat capacity of the sample in the ampoule was determined from the expression:

$$c(T_2)=\frac{1}{m}\left(\frac{k_T(T_2)(T_1-T_2)}{b_1}-C_a\right),$$

where m – mass of the sample; k_T – the constant of the heat meter; C_a – the heat capacity of the ampoule; b_1 – heating rate; T_1 and T_2 – the temperatures of the top and the lower surfaces of the heat meter, respectively.

The error of the heat capacity measurement with the help of the modernized IT-c-400 is mainly due to the heating rate, with an assumption, that all other destabilizing factors are taken into account and stabilized.

The software for the modernized device is developed in LabView 2009 has a modular configuration and performs the following functions:

1) input of the initial data: the date of the experiment, the material name, the sample number, the number of the experiment, the operator name;

2) calibration of the device in order to determine the constants for the calculation dependences;

3) control of the experiment process and experimental data processing;

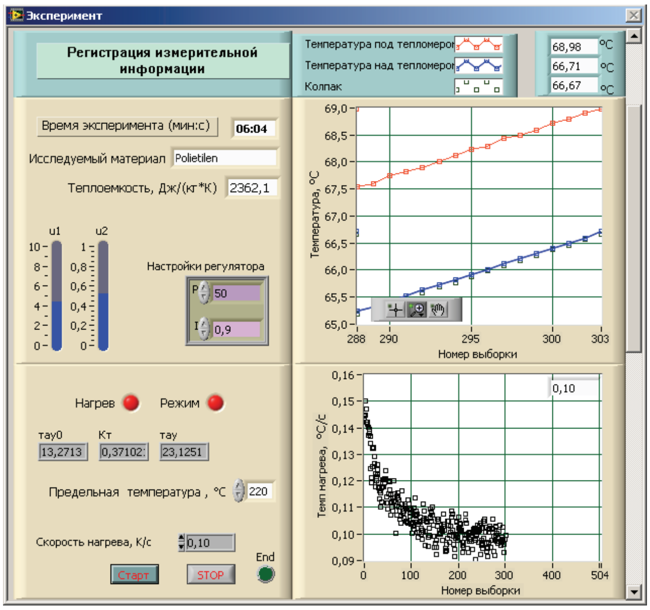
4) storage and visualization of the experimental results.

The control panel of the respective module of the experiment is shown in the Fig. 2.

To determine the thermal conductivity of the materials depending on the temperature the automated measurement setup, which is a modernized thermal conductivity measurer IT-λ-400, was used. This device allows determining the thermal conductivity of both solid and liquid polymers. The measuring cell (Fig. 3) was made to allow the investigation of liquids. It includes an ampoule *2* with a copper bottom and walls of the heat-resistant polymer (polyetheretherketone), placed on a copper plate *1*. The test material is placed in the ampoule, and the rod *5* is set on the top, on the thermocouple tubes *3* and fixed at a predetermined height by screws *4*. To ensure the correct position of the rod *5,* the disc of the polymethylmethacrylate with a known thickness is used and placed in the ampoule *5* under the rod. After that, the screws are screwed into the rod holes up to their contact with the thermocouples tubes *3*. In this way, after removing the disc from the ampoule and filling it with test liquid, we will have the known thickness of the liquid layer between the rod *5* and the bottom of the ampoule.

The measuring unit of the device (see. Fig. 4) includes a heater *5*, the heat flow from which directs through the heat meter with the heat flow transducer *9* and the contact copper plate into the ampoule with the investigated sample (liquid) *1* and after that into the rod *5*. The protective cover *3* with the heater *4* form the adiabatic shell to prevent the heat exchange between the measurement object and the environment.

During the experiment the temperature of the shell was maintained at a temperature of the rod by changing the power of the heater depending on the thermo-emf. differences of transducers *6* and *9* in accordance with the PID control law. Additionally, the temperature of the rod and copper plate *3,* the heat flow were registered and measured, respectively, by the transducers *2*, *7* and *9*. The heating rate of the sample was kept constant, and could be adjusted in the range 0.2–0.02 K/s by controlling the power of the heater *1*. Connecting transducers and amplifiers was made by a personal computer in the same way as in the case with the IT-λ-400 device (Fig. 5). Calculated dependences for the thermal conductivity determination corresponded to the method described in [8] (the same as for non-upgraded device dependencies).



68,98 °С
66,71 °С
66,67 °С

Время эксперимента (мин:с) 06:04
Исследуемый материал Polietilen
Теплоемкость, Дж/(кг*К) 2362,1

Настройки регулятора
P 50
I 0,9

Нагрев ●
Режим ●

тау0 13,2713
Кт 0,37102:
тау 23,1251

Предельная температура , °С 220

Скорость нагрева, К/с 0,10

Fig. 2. The control panel for experimental determining the dependence of the investigated material heat capacity on temperature

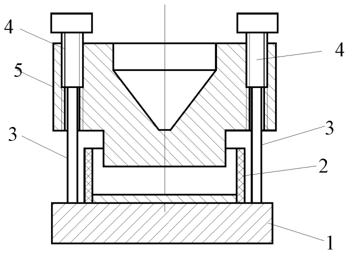


Fig. 3. The scheme of the measurement cell of the modernized device ИТ-λ-400

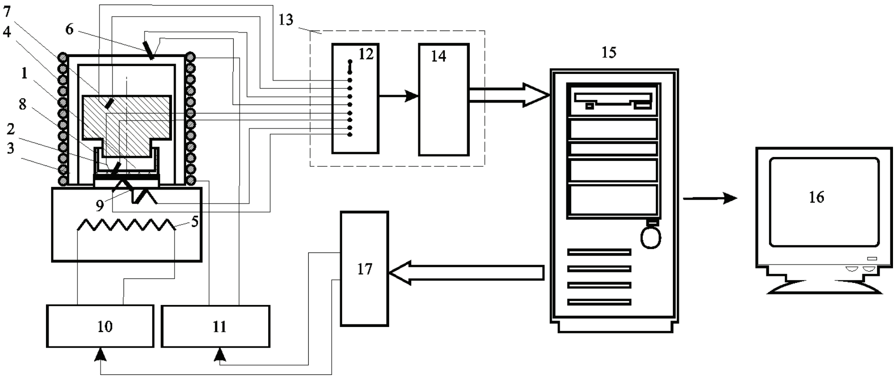
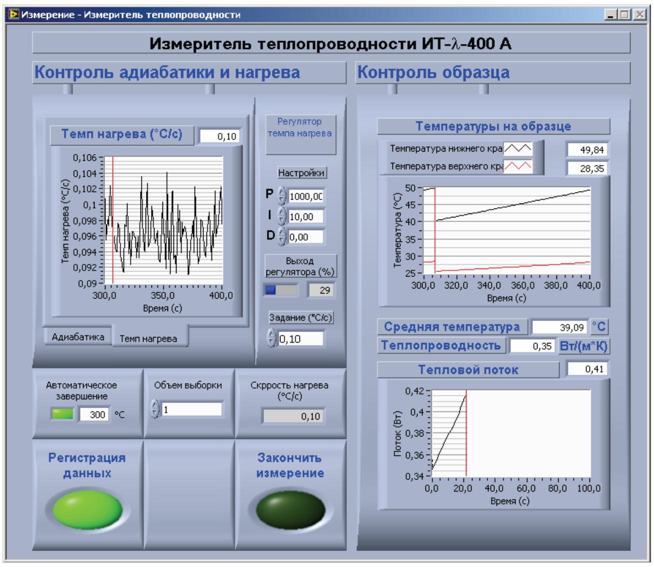


Fig. 4. The functional scheme of the modernized device ИТ-λ-400



Темп нагрева (°C/c) 0,10

P 1000,00

I 10,00

D 0,00

Выход регулятора (%) 29

Задание (°C/c) 0,10

Температура нижнего кра 49,84

Температура верхнего кра 28,35

Средняя температура 39,09 °C

Теплопроводность 0,35 Вт/(м*К)

Тепловой поток 0,41

Автоматическое завершение 300 °C

Объем выборки 1

Скрросто нагрева (°C/c) 0,10

Fig. 5. The front panel of the measurement module

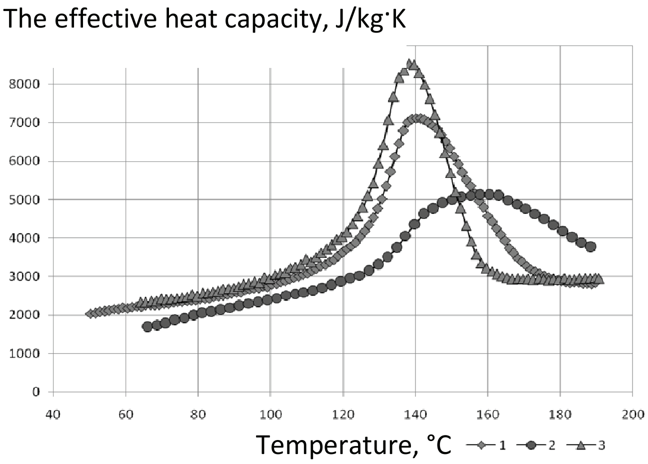


Fig. 6. The dependence of the effective polyethylene heat capacity on temperature obtained for different heating rates:
1 – heating rate 0,1 K/s; *2* – heating rate 0,2 K/s;
3 – heating rate 0,05 K/s

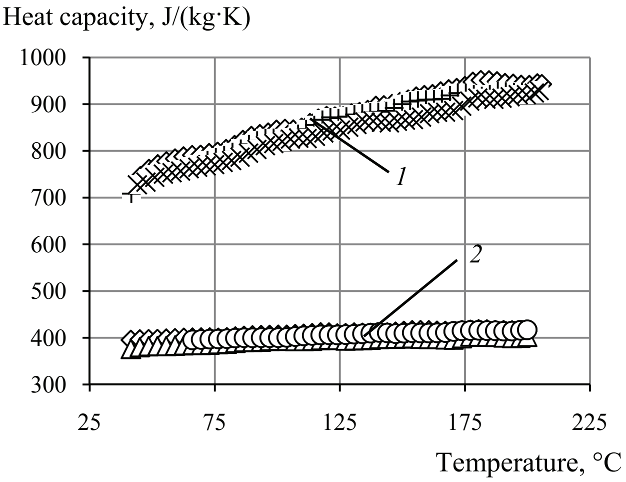


Fig. 7. The dependence of the heat capacity on temperature:
1 – quarts glass; *2* – copper

Determination of the Measurement Error

There are many factors which influence the result of the heat capacity (as well as thermal conductivity) measurement. The main factors are:

1. *The heating rate of the sample.* With the increase in the rate of the material heating the temperature difference in the sample increases and, therefore, the error of the thermophysical properties determination occurs.

2. *Thermal contact resistance under measuring the thermal conductivity and heat capacity of solid samples.* To reduce the influence of this error source the surface of the samples should be carefully prepared preventing their concavity, convexity and roughness worse than Rz 0,63. For samples in the form of pastes and liquids, this source of error is absent.

3. *The error of measuring the temperature by thermoelectric transducers.* Since the temperature difference is measured in the experiment, the systematic error of thermocouples can be neglected. Random error in this case is low due to the use of the data acquisition boards with 24-bit ADC. The quantization error of such ADC does not exceed 4×10^{-6} V, which corresponds to an error of temperature measurement 10^{-3} °C.

The numerical calculations [7] show that under determining the dependence of heat capacity on the temperature, the heating rate should not exceed 0.1 K/s. This fact was confirmed in experiments with polyethylene UHMWPE (results of the experiments are shown in Fig. 6). As we can see, with increase in the heating rate the measured value of the heat capacity decreases and the height of the thermogram peaks (which corresponds to polyethylene melting) decreases while their width increases.

To assess the heat capacity measurement error more accurately, series of calibration experiments were carried out using standard samples (quartz glass and copper). Graphs of the measured heats capacity values dependences on the temperature at the heating rate of 0,1 K/s are presented in the Fig. 7 and Table 1.

Using the lower heating rates is undesirable because of the increase in the duration of the experiment and the rise in the error of measuring the temperature difference in the heat meter, due to the heat flow reduction.

To determine the thermal conductivity measurement error the calibration experiments were carried out with optical quartz samples (GOST 17622-72) and glycerol.

Experiments with liquid glycerol were performed using the upgraded measuring cell (see. Fig. 3), and with samples of the quartz the standard rod of the measurement cell was used without the ampoule.

Table 1

The results of calibration for quarts

Temperature, K	The measured heat capacity, J/(kg·K)			The actual heat capacity value, J/(kg·K)	Root-mean-square deviation, J/(kg·K)	Range, J/(kg·K)
	c_1	c_2	c_2			
330	764	763	803	780	22.8	40
350	797	781	813	808.1	16	32
370	838	824	835	834.8	7.4	14
390	865	845	869	860.1	12.9	24
410	892	873	898	883.9	13.1	25
430	918	882	919	906.1	21.1	37
450	921	918	954	926.8	19.9	36
470	935	930	951	946.1	11.0	21

Experiments have shown that the measurement error of thermal conductivity for both liquid (glycerol) and solid samples does not exceed 7 % (for confidence probability = 0.95).

Results and Discussion

The 8 % graphene paste in water and glycerol was the object of the study. Immediately before measuring the probe, a sample was taken from the container with the investigated material. After its mass was determined with an accuracy up to ±1 mg, the material was placed into the ampoule with a specially designed scoop and the residue was weighed. According to the mass difference before and after the loading, the material in the ampoule was weighed and it was equal to 1.7–1.8 g. The results of determination of the samples heat capacity and thermal conductivity dependence on the temperature are shown in Fig. 8 and Fig. 9. The measurement error does not exceed 7 %.

A sharp increase in heat capacity of graphene paste on the water base at temperatures above 100 °C can be explained by heat effect (heat absorption) at water evaporation from the paste. Therefore, such an increase in heat capacity appears to be apparent. Heat capacity of the graphene paste on the base of glycerol was found to be significantly smaller than that of the water-based paste and more resistant to temperature effects.

The thermal conductivity of pastes on the basis of the polygraphene and water was higher than for the pastes based on polygraphene and glycerol (Fig. 9), but the latter has wider temperature range of use (up to 230 °C).

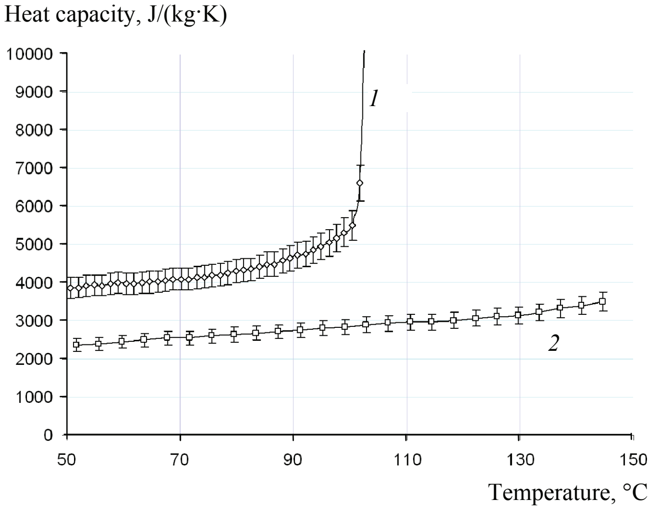


Fig. 8. The dependence of heat capacity on temperature of the 8 % polygraphene suspension on the base of:
1 – water; *2* – glycerol

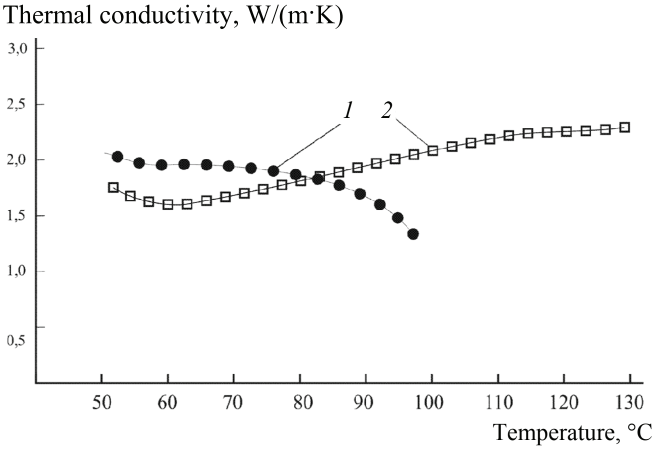


Fig. 9. The dependence of thermal conductivity on temperature of the 8 % polygraphene suspension on the base of:
1 – water; *2* – glycerol

Conclusion

The thermal conductivity of pastes based on oxidized graphene with water and glycerol is quite high (about 1, 2–2.5 W/(m·K)). This allows to use them to reduce the thermal contact resistance at the heat dissipation from the heating surface. The experimental data on the heat capacity dependence on temperature presented in the paper should be used in numerical and analytical calculation of temperature fields in the system of contact bodies where a thin layer of paste is located between the layers.

It should be noted that the temperature dependence of heat capacity of glycerol-based paste is more significant, while the heat capacity of the water-based paste is much higher, however, the temperature range of its use does not exceed 100 °C.

References

1. Graphene nanoplatelets [Electronic resource]. Access mode: http://nanotc.ru/index.php/producrions/85-gnp, free. (The request date: 03/06/2015).

2. Tkachev, A.G., Melezhik A.V., Dyachkova T.P., Blokhin A.N., Burakova E.A., Pasko T.V. (2013) Uglerodnyye nanomaterialy serii «taunit»: proizvodstvo i primeneniye [The series of carbon nanomaterials "Taunit": production and use] (Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya [News of Higher Schools. Chemistry and chemical technology], 56 (4), 55-59. (Rus).

3. Platunov E.S., Burawoy S.E., Kurepin V.V., Petrov G.S. (1986). Teplofizicheskiye izmereniya i pribory [*Thermophysical measurements and instrumentation*]. L.: Mashinostroyeniye, 256 p. (Rus).

4. Divin A.G., Mishchenko S.V., Ponomarev S.V., Mozgova G.V., Tkachev A.G. (2008). An automated measurement setup for studying the dependences of the thermal conductivity and rheological characteristics of non-newtonian fluids on the shear rate. *Instruments and Experimental Techniques,* Vol. 51, No. 3, pp. 480-488.

5. Ponomarev, S.V., Mishchenko, S.V., Divin, A.G., Vertogradskiy, V.A., and Churikov, A.A. (2008). Teoreticheskiye i prakticheskiye osnovy teplofizicheskikh izmereniy [The theoretical and practical fundamentals of thermophysical measurements]. Moscow: Fizmatlit, 81-199. (Rus).

6. Belyaev V.P., Belyaev M.P., Mishchenko S.V., Belyaev P.S. (2014). The design of a measuring instrument for determining the diffusion coefficient of solvents in thin articles made of capillary-porous materials. Measurement Techniques, Vol. 56, No. 10, pp. 1190-1196.

7. Divin A.G. (2013). Metody i sredstva dlya opredeleniya zavisimosti teplofizicheskikh kharakteristik zhidkikh polimernykh materialov ot skorosti sdviga i temperatury [Methods and means for determining the dependence of the liquid polymeric materials thermophysical characteristics on the shear rate and temperature : abstract of doctoral dissertation, Tambov State Technical University. (Rus).

Functional Nanomaterials of Hyperfine Liquids Cleaning and Gases Aerosol Filtration

Designated purpose, application area

High performance microfiltration of liquids from the micron and submicron particles and superfine cleaning of gas environment from suspended aerosol particles.

Originality, uniqueness

The project research objective is efficient technologies development of nanocarbon modification of standard filter materials in order to intensify the filtration process through the creation of porous permeable layer on the surface of filter fibers. Process of such filter structure development presupposes insignificant pressure drop and trapping increase.

The methods of nanocarbon modification of high temperature filter materials (ceramics, pyroceram, metals), activated carbons, sorbents and synthetic polymer membranes are developed. Number of formation parameters of porous permeable membranes of carbon nanomaterials on the modified materials surface are studied and the prototypes with improved characteristics are obtained.

There are three results of intellectual activity.

Specifications

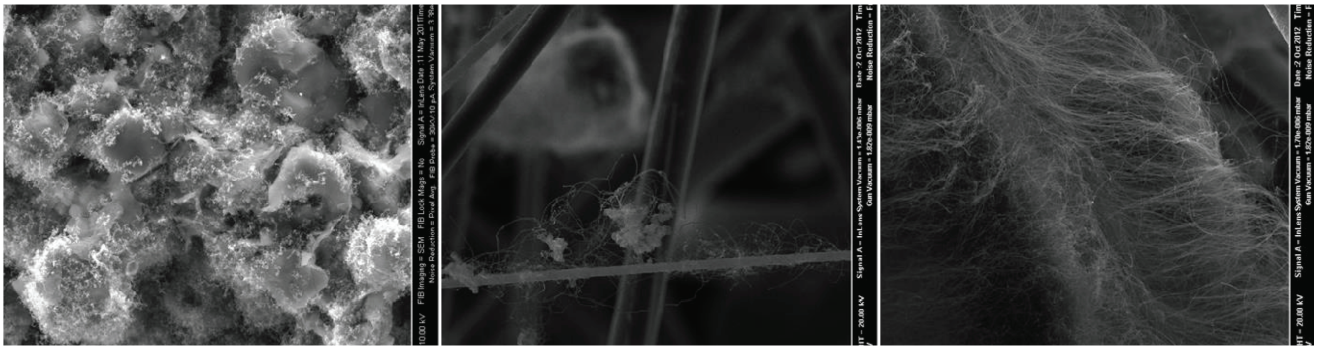
The characteristics, obtained by this technology of synthesis of carbon nanomaterials “Taunit” are determined by customers’ demand.

Prototypes with improved quality based on inorganic fibers (siliceous, ceramic, glass-ceramic, etc.) coated with the porous structure of the synthesized carbon nanotubes with specific parameters are obtained.

Patent documentation

Patent RF № 2411069 “Modifying Method of Inorganic Membrane Porous Structure by Carbon Nanomaterial”. Authors: Tkachev A.G., Burakov A.E., vanova I.V., Burakova E.A.

Patent RF № 106253 “Reactor for Carbon Fiber Structures Obtaining by Catalytic Pyrolysis”. Authors: Tkachev A.G., Burakova E.A., Kobtseva Y.A., Ivanova I.V., Burakov A.E.



Tambov State Technical University
Department “Technology and Methods of Nanoproducts Manufacturing”, LtdLC “Nanofilter”,
NRC “Kurchatov Institute”
Contact person: Candidate of Technical Sciences **Burakov Alexander Evgenyevich**
Tel.: +7 920 232-77-35. E-mail: m-alex1983@yandex.ru