Experimental Determination of the Thermophysical Properties of Polygraphene-Based Pastes

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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 researchers all over the world has been concentrated on such a modification of carbon as graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allotrope of carbon―graphene. This is a two-dimensional allo
Fig. 1. The functional scheme of the modernized IT-c-400 heat capacity measuring device

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) 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:

\[ c(T_2) = \frac{1}{m} \left( \frac{k_f (T_2) (T_1 - T_2)}{b_1} - C_a \right) \]

where \( m \) – mass of the sample; \( k_f \) – 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).

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 IT-λ-400

Fig. 4. The functional scheme of the modernized device IT-λ-400
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 $4 \times 10^{-6}$ 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.

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.
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 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**


There are three results of intellectual activity.

### 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.

### 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

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