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Article

Polymer nanocomposites doped with nanocarbon

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Abstract: Possibilities of usage of polymer materials are expanded considerably as a result of the addition of nanocarbon particles (carbon nanotubes, graphene, graphene oxide, and nanostructured graphite). The article contains the consideration of several examples of producing and practical applications of polymer-based composites doped with nanocarbon particles. Such particles possess high electric and thermal conductivity; therefore, the usage of nanocarbon additives permits one to obtain polymer-based composite materials with enhanced transport characteristics. Polymers doped with carbon nanoparticles exhibit percolation conduction so that the charge transport proceeds by a limited number of percolation paths formed by contacting particles. Imperfection of contacts determines the non-linear character of the conduction of such composites: the resistance decreases with the applied voltage increase. The thermal conductivity of nanocarbon particles exceeds that for polymers by 4–5 orders of magnitude; therefore, even a small additive of nanocarbon (on the level of several percent) permits one to get a polymer material with enhanced thermal conductivity. Nanocarbon-doped composites find application particularly as phase change materials, which are able to accumulate and release considerable thermal energy as a result of the phase transition. One more direction of the usage of nanocarbon-doped composites relates to the development of the optical sensor on the basis of carbon nanoparticles. In this device, amplification of the Raman signal, bringing information on the chemical composition and structural characteristics of an object, is reached as a result of the interaction of electromagnetic radiation with plasmon oscillations of conducting nanoparticles.

Keywords: carbon nanotubes; graphene; percolation conduction; thermal energy accumulator; Raman scattering; optical sensor

1. Introduction

Considerable recent attention from researchers and engineers has been paid to the development of polymer composites doped with nanocarbon particles. This is caused by a possibility of a considerable change in physical and chemical characteristics of polymers due to nanocarbon particles additive and in expansion of the application region of such materials. Usually carbon nanotubes, graphene, and partially reduced graphene oxide are considered as nanocarbon additives to polymers. Such particles are characterized by a high electric and thermal conductivity, so that the usage of nanocarbon additives permits one to obtain composite materials with enhanced transport properties. A lot of publications are devoted to the development of nanocarbon-doped polymer composites. Some of these publications were reviewed, in particular in articles [1–4].

Polymer-based conducting composites find their application at fabrication of aircraft tires for which the existence of a conducting additive is a critical issue, because it permits one to avoid the static charge on the tire surface creating a possibility of an accident. The thermal conductivity of nanocarbon particles exceeds that for polymers by 4–5 orders of magnitude, therefore even a small additive (on the level of several percent) permits one to produce polymer materials with enhanced thermal conductivity. Polymer-based composites doped with nanocarbon particles find their application, in particular, as phase change materials which are able to accumulate and release a considerable thermal energy in result of the phase transition. One more direction of the usage of nanocarbon doped composites relates to the development of the optical sensor on the basis of carbon nanoparticles. In this device the Raman signal bringing the information on the chemical composition and structural characteristics of an object is amplified as a result of the interaction between electromagnetic radiation and plasmon oscillations of conducting nanoparticles.

One should note that the preparation of nanocarbon-doped composites meets some difficulties related to a trend of carbon nanoparticles to aggregation. This trend prevents a homogeneous distribution of nanoparticles over the volume the composite. Many tools can be used to overcome this trend, such as centrifugation, ultrasonication and functionalization of nanoparticles with various radicals. The problem of providing a homogeneous distribution of nanoparticles has not yet resolved entirely, and many laboratories address their activity in this direction.

Polymer-based composites doped with carbon nanoparticles can be used in various devices and technologies. These composites possess percolation conduction, so that the electric current flows along percolation paths formed by contacting nanoparticles. The resistance of the composites is caused by contacts between the particles which determines non-linear, non-Ohmic character of conduction.

The present article contains a consideration of the above-mentioned issues, related to properties of conducting polymer composites and their technology applications.

2. Percolation conduction of polymer composites doped with carbon nanotubes

Carbon nanotubes (CNTs) possess metal or semiconductive properties, depending on their structure, therefore inserting such particles into non-conducting polymer material imparts conducting properties to this material. At a low concentration of CNT additive the conduction of the composite has percolation character. Therewith the charge transport proceeds through paths formed by a chain of contacting nanotubes. The percolation conduction has the threshold character, so that exceeding the threshold content of an additive result in a sharp conductivity jump. The position of the percolation threshold is inversely proportional to the aspect ratio (ratio of the length to the diameter) of additive particles, therefore for CNTs, having the aspect ratio up to 10^4 the threshold content can be as low as 0.01% (by weight). The conductance of a percolation chain consisted of CNTs depends considerably on the contact resistance between neighboring nanotubes. Such a contact is not perfect as a rule so that the charge transport proceeds as a result of tunneling electrons between neighboring nanotubes, The tunneling probability depends exponentially on the size of the gap and on the potential difference between the nanotubes. For this reason the resistance of a percolation chain determining the conductance of a composite turns out to be dependent on the applied voltage. Thus polymer composites doped with CNTs possess non-linear current-voltage characteristic.

The Non-Ohmic character of conduction of polymer composites doped with CNTs has been studied theoretically in [5]. In this work electron tunneling through the barrier formed by nanotubes spaced by the distance μ from each other is described using the standard quasiclassical approach. **Figure 1** compares the calculation results obtained assuming the normal distribution of the parameter μ with dispertion σ and experimental data obtained in [6,7]. As is seen, a good agreement between calculated and measured data is observed at a proper choice of parameters μ and σ. In these calculations the number of contacts $n = 1000$, the values μ, σ are shown on the figure. Experiment: A—high pressure polyethylene (HPPE) + 7% (by weight) multi-layer CNTs, $T = 300\ K$; B—(HPPE) + 5% CNTs, $T = 300\ K$; C—(HPPE) + 7% CNTs, $T = 200\ K$; D—(HPPE) + 5% CNTs, $T = 200\ K$ [6]; E—polyvinilbutiral (PVB) + 3% CNTs; F—polydimethylsiloxane (PDMS) + 1% CNTs [7].

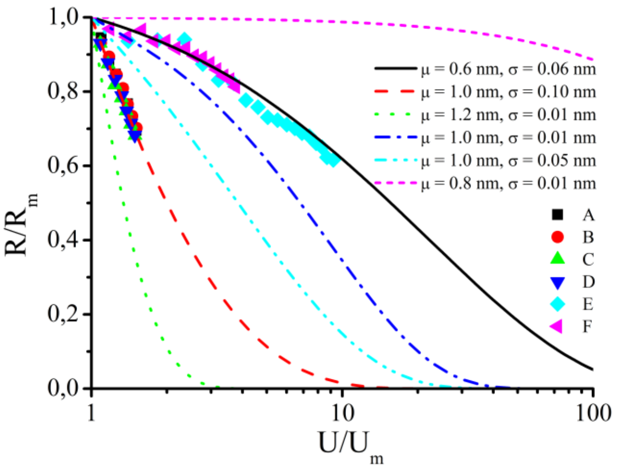

Figure 1. Comparison of calculated in [5] dependence of the resistivity of nanocomposites doped with CNTs on the applied voltage with those measured in [6,7] (relative units).

The conductivity of CNT-doped polymer-based composites was measured in a plethora of works (see, for example, the reviews [1,2]). However results of such measurements are indicated usually without the value of the applied voltage. Therewith the non-linear character of composite conduction is neglected, so that the conductivity values shown in articles hardly give the adequate notion on the properties of composites.

3. Phase change materials with enhanced thermal conductivity

Phase change materials (PCM) are able to accumulate and release a considerable thermal energy in result of the phase transition. Due to this ability PCM find their application in buildings for decreasing the amplitude of temperature oscillations inside rooms under the action of the environment (see, for example [8,9]), for stabilization of the temperature in electronic facilities and complicated setups [10], for accumulating the energy produced by solar or wind energy plants [11] etc. Wide spread of PCM in building, energy and other fields is hindered by the problem related to a rather low thermal conductivity of the most of PCM (on the level of 0.2 W/m K). Due to this peculiarity devices containing PCM possess high inertia which impedes the thermal exchange between the environment and the working fluid. To overcome this problem there is used an additive from nanocarbon particles that have the thermal conductivity coefficient 4–5 orders of magnitude exceeding that for PCM. Such an approach permits one to enhance considerably the thermal conductivity of a polymer-based composite. Thus inserting as low as 1% (by weight) graphene into polyvinilene fluoride results in about 15-fold enhancement of the thermal conductivity [12].

The possibility of production of a PCM with enhanced thermal conductivity permits one to use these materials as a basis for a thermal energy accumulator. **Figure 2** presents one of possible configurations of such an accumulator [13]. The accumulator has the module structure, i. e. it is consisted of a some number of similar modules. Such a structure permits one to enhance the energy storage of the system just increasing the number of modules. Two cylindrical concentric pipes with radius R_1 R_2 inserted each into another form the basis of a module. The inner pipe is fabricated from copper to facilitate the thermal exchange between water and PCM. The outer pipe is fabricated from a plastic (polypropylene) having rather low thermal conductivity to avoid leaking thermal energy into environment. The space between the outer and inner pipes is filled with PCM, while water which is used as a working fluid is passed through the inner pipe. Thermocouples are inserted into the PCM volume to control the temperature in the process of the thermal exchange.

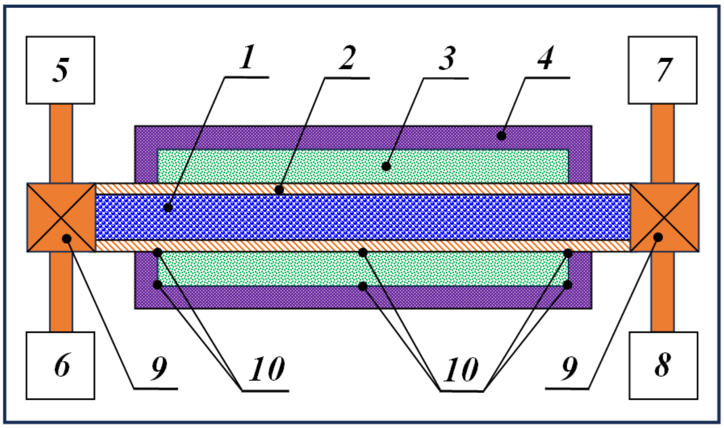

Figure 2. Configuration of a thermal energy accumulator on the basis of PCM [13]. 1—hot or cold water flow; 2—copper pipe for water supply; 3—hollow between the inner and outer pipes filled with PCM; 4—outer pipe fabricated from a plastic; 5—cold water supply; 6—hot water supply; 7—hot water output; 8—cold water output; 9—water valves; 10—thermocouples.

Passage hot water through the conduit promotes heating the PCM and the phase transition in result of which the material is melted and transforms into the liquid state. Therewith it accumulates the phase transition energy that can be extracted passing cold water through the conduit. Cooling PCM promotes the phase transition which results in heating the water up to the temperature close to the phase transition point.

The dynamics of the thermal exchange between the working fluid (water) and PCM with different thermal conductivity coefficient has been established by means of the code COMSOL MULTIPHYSICS [13,14]. **Figure 3** presents the dependences of the characteristic thermal exchange time on the thermal conductivity coefficient of PCM calculated for heating and cooling regimes. The characteristic thermal exchange time is defined as the time for which 95% PCM is subjected to the phase transition. The calculations were performed assuming that as a PCM is used paraffin P2 having the phase transition point (melting) 55 °C, specific phase transition enthalpy 212 J/g, specific thermal capacity 2.1 J/g and thermal conductivity $\lambda = 0.21\ \mathrm{W/m \cdot K}$.

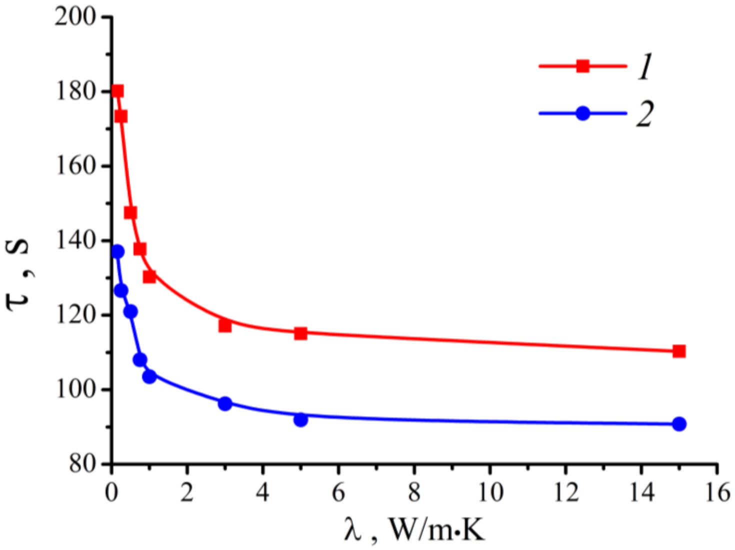

Figure 3. Dependences of the characteristic thermal exchange time on the thermal conductivity coefficient of PCM calculated for heating (1) and cooling (2) regimes [13,14].

As is seen from the dependences shown on **Figure 3**, the thermal exchange time is shortened sharply at the enhancement of the thermal conductivity coefficient from 0.2 to ~3 W/m K. Saturation of these dependences caused by the influence of the convective thermal exchange indicates the minimum value of the thermal exchange time which is reached at the thermal conductivity coefficient at the level of 5 W/m K. Further enhancement of the thermal conductivity results in only minor change of the thermal exchange time. This result implies the existence of the optimal quantity of nanocarbon additive providing the maximum effect of thermal exchange facilitation.

4. Production of graphene by thermal reduction of graphene oxide

For a wide spread of PCM with enhanced thermal conductivity one should possess a large quantity of nanocarbon material used as an additive. Experiments and model calculations [12] imply that the most proper additive to PCM is graphene, a small quantity of which (~1 %) is sufficient for 15-fold enhancement of the thermal conductivity. There with a high quality and defect less structure of graphene is hardly necessary requirement. Thereby the necessity in usage of such time-expensive and low productive approaches as micromechanical exfoliation of graphite and CVD is dropped out. More productive approaches, providing the graphene production in a macroscopic quantity but of lower quality are based on chemical or thermal reduction of graphene oxide. Therewith for production of graphene oxide is used the Hummers method [15] providing a macroscopic quantity of the material. The chemical method of the graphene oxide reduction requires for the usage of toxic or ecologically harmful reagents such as hydrazine N_2H_4, therefore more proper approach to the large scale production of graphene is seemed the thermal graphene oxide reduction. According to this approach, graphene oxide samples are subjected to the thermal treatment at a temperature up to 800 °C. The thermal treatment results in removal of radicals attached to the graphene surface.

The dynamics of thermal reduction of graphene oxide was studied, in particular, in [16,17]. The degree of the graphene oxide reduction was registered by measuring the electric conductivity of the material which is very low for graphene oxide and is enhanced as the reduction proceeds. **Figure 4** shows the dependence of the conductivity of a graphene oxide sample on the thermal treatment temperature. As graphene oxide samples were used paper—like sheets of 30–60 μm in thick, 10–15 mm in width and 15–25 mm in length. The material's density accounted 1.2 g/cm^3. The material consisted of graphene oxide flaxes of 10–30 μm in size. As is seen from the dependence shown on **Figure 4**, the conductivity of the material enhances sharply within the range of the treatment temperature 100–200 °C, which is a result of the graphene oxide thermal reduction. The jump in the conductivity can be considered as the percolation transition which occurs at the condition when the thermally reduced graphene oxide flaxes form the conducting path. In distinction of the traditional percolation transition, occurring at exceeding some value of the additive content, in this case the reason of the percolation transition is imparting conducting properties to graphene oxide flaxes contacting with each other.

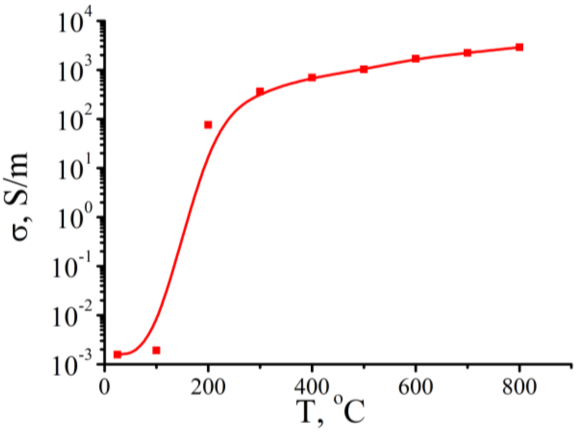

Figure 4. Dependence of the conductivity of graphene oxide samples on the thermal treatment temperature [16,17].

The graphene oxide reduction accompanying with removal of attached radicals results in lowering the density of the material. **Figure 5** presents the dependence of the density of thermally reduced graphene oxide samples on the thermal treatment temperature. As is seen, the density of the material subjected to the thermal treatment at 800 °C, accounts about 0.5 g/cm^3. This corresponds to the average distance between neighboring flaxes about 1.5 nm which exceeds by 4.5 times that for crystalline graphite. This permits one to conclude that the conductivity of the material accounted for one layer comprises about 1800 S/m. This is about twice lower than the reference value of the crystalline graphite conductivity. Such a discrepancy is caused by rather small size of flaxes making up the material. The conductivity of such a material is determined by not only the conductivity of those flaxes which is close to the graphene conductivity, but also by the contact resistances that lower the conductivity of reduced graphene oxide.

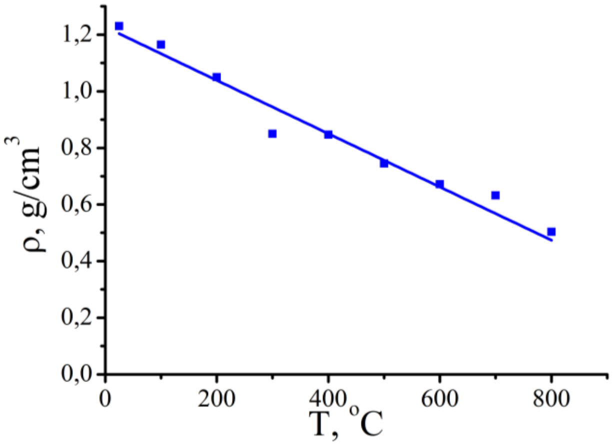

Figure 5. Dependence of the density of graphene oxide samples on the thermal treatment temperature [16,17].

5. Optical sensor on the basis of nanocarbon particles

Raman spectroscopy is an effective tool for analysis of the chemical composition and structural characteristics of molecules and materials. The main drawback of this diagnostic tool relates to a rather low intensity of Raman signal, which limits the possibility of its usage and does not permit one to determine the content of minor additive in objects under investigation. This drawback is overcame in result of the usage of the effect SERS (Surface Enhanced Raman Scattering) discovered by the British chemist Fleishman in 1974 [18]. According to this discovery, the Raman signal is enhanced greatly, when the object under investigation is placed near conducting particles or nanostructured metal surface. For this aim used usually noble metals (Au, Ag, Pt) and metals possessing high electric conductivity (such as Cu, Li, Na, K, In, и Rh). The SERS mechanism relates to surface plasmon oscillations of electrons in metals, which amplify the electromagnetic field acting onto the molecules under investigation and, correspondingly, enhance the Raman signal. Early publications devoted to SERS were reviewed, in particularly, by Moskovits [19] and Nabiev et al. [20], while the recent works are reviewed by Pilot et al. [21]. The amplification factor of the Raman signal enhanced by SERS reaches values ~10^{14} [22], which offers a possibility for determination of not only minor admixtures in a material but even single molecules [23,24].

The SERS effect can be used as the basis for an optical sensor for determination of the composition of materials and the content of minor admixtures. Such a sensor is in demand in biology and medicine, where the registration of minor molecular admixtures can be used for the diagnostics of various deceases including cancerous ones. **Figure 6** presents a possible configuration of such a sensor. In this device nanocarbon particles (carbon nanotubes, graphene) are used as a sensitive element. Advantages of such particles in comparison with metal nanoparticles relate to their miniature sizes and high thermal, chemical and mechanical stability of nanocarbon. The basis of the sensor in an optical waveguide, the surface of which is covered by a thin layer of a transparent polymer material (for example, epoxy resin) containing nanocarbon particles. The waveguide of 50–100 μm in diameter is inserted into a cavity of a human or another object. Laser beam is directed through the waveguide onto the region containing the molecules to be registered. Interaction of the laser beam with the molecules under investigation results in the appearance of the Raman signal containing the information on the vibration spectrum of the molecules. This signal is enhanced due to the presence of nanocarbon particles (nanotubes, graphene flaxes). Thereby the presented sensor permits one to perform a not invasive analysis of the chemical composition and structural characteristics of molecules contained in internal cavities of a living creature.

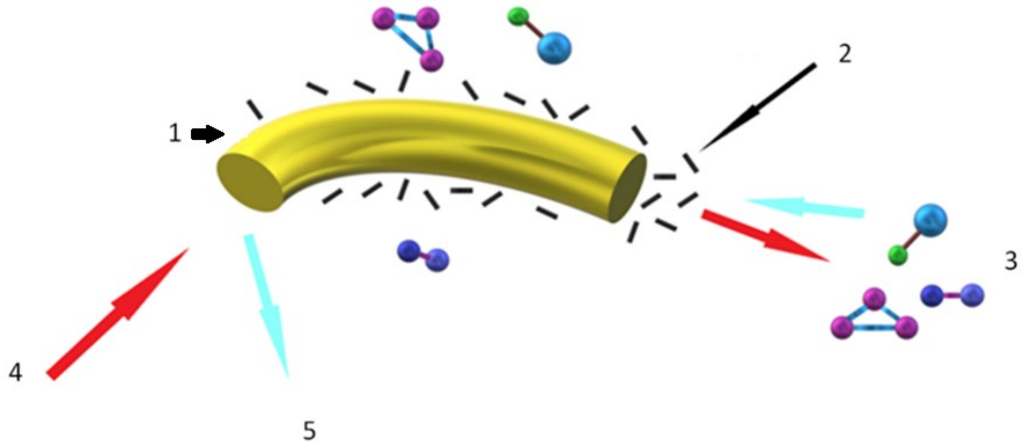

Figure 6. Schematic representation of the configuration of the optical sensor. 1—optical waveguide; 2—nanocarbon particles; 3—the object under investigation; 4—laser beam; 5—scattered signal.

The possibility of the development on an optical sensor on the basis of nanocarbon particles is based on the experimental results [25] demonstrating the effect of the Raman signal enhancement in the presence of carbon nanotubes. These results have been presented on **Figure 7** showing the Raman spectrum of water in the absence and in the presence of carbon nanotubes of various concentrations. As is seen a considerable amplification of the Raman signal occurs in the case when the density of arrangement of nanotubes on the substrate surface is rather low, so that the effect of screening of the electromagnetic field by neighboring nanotubes is practically negligible.

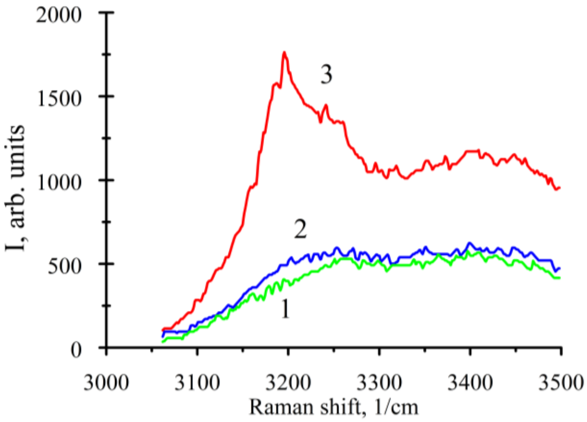

Figure 7. Raman spectra of water: CNTs are absent (1); high concentration of CNTs (2); low concentration of CNTs (3) [25].

The amplification factor of the Raman signal by a single nanotube G_{SERS} in the experiment [25] can be estimated on the basis of the following relation [21]

$$G_{SERS} = (P_{SERS} N_{Raman} / P_{Raman} N_{SERS}) / N_{CNT} \tag{1}$$

where P_{SERS} and P_{Raman} are the intensities of the normal and enhanced Raman signal, N_{Raman} is the number of water molecules irradiated by the optical radiation and N_{SERS} is the number of water molecules the Raman signal of which was experienced by the enhancement effect, N_{CNT} is the number of nanotubes placed onto the substrate surface covered by the water droplet. In accordance to the experimental results presented on **Figure 7**, the ratio $(P_{\mathrm{SERS}}/P_{\mathrm{Raman}}) \approx 3$. As is shown by the authors of Ref. [26], the enhancement of the Raman signal occurs at the condition when the molecules under investigation (in the present case water molecules) are spaced no more than $d \approx 40$ nm from the enhancing object (in the present case, nanotubes). Thereby the volume of the substance experienced by the SERF effect accounts

$$V_{SERS} = \pi(d^2 - R_{CNT}^2) \cdot L \cdot N_{CNT}/3 \tag{2}$$

where RCNT ≈ 10 nm is the average radius of nanotubes, L ≈ 1 μm is their average length. The estimation (2) assumes that only nanotubes with the armchair structure possess conductive properties and the number of such nanotubes accounts 1/3 of the total quantity. For the estimation of the nanotubes quantity lying on the substrate surface covered with water we will believe that these nanotubes are arranged on the surface in an arbitrary manner and do not contact with each other. Taking into consideration that the area of this surface accounts about $S \approx 0.1$ cm^2, one obtain the estimation of the minimum quantity of nanotubes placed on the substrate surface covered with the water droplet

$$N_{CNT} \approx S/L^2 \approx 3 \cdot 10^6 \tag{3}$$

Taking into account the relation (1), this results in the following estimation of the amplification factor of the Raman signal by a single nanotube

$$G_{SERS} \approx 10^7 \tag{4}$$

The real value of N_{CNT} is less that the above-given quantity (3), because some part of nanotube are in contact with each other and do not contribute into the amplification of the Raman signal. Thereby the estimated magnitude of the amplification factor (4) should be considered as a lower estimate so the true value of the amplification factor exceeds the above-given quantity (4).

Experiment [25] has shown that carbon nanotubes can be used as a tool for the enhancement of the Raman signal. The above-performed estimation implies that the signal amplification factor reaches 10^7. For this purpose can be also used graphene flaxes possessing the electron conduction, as is known. This possibility is confirmed by the results of experiment [27], where electron plasmon oscillations in thermally reduced graphene oxide samples were observed. **Figure 8** presents the dependences of the conductivity and plasmon peak intensity on the thermal treatment temperature [27]. As is seen, the enhancement in the thermal treatment temperature is accompanied with an increase in the conductivity of samples and in the intensity of the plasmon peak. This indicates the possibility of the usage of thermally reduced graphene oxide as a tool for the enhancement of the Raman signal.

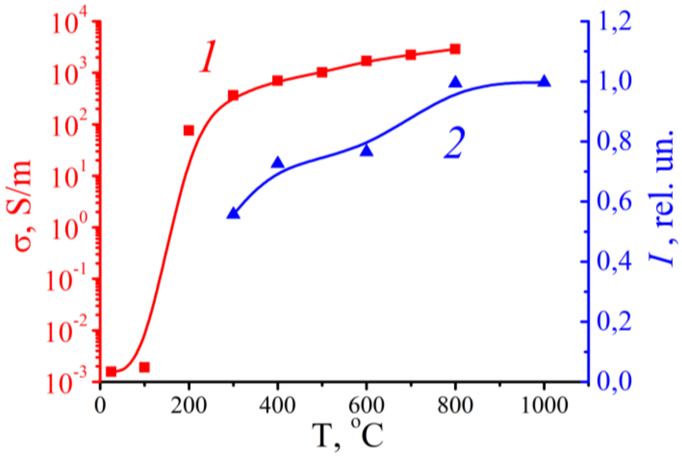

Figure 8. Dependence of the conductivity 1 and intensity of the plasmon peak 2 of thermally reduced graphene oxide on the treatment temperature [27].

6. Conclusion

Polymer composites doped with nanocarbon particles possess unique properties, which permit one to use them in a wide field of scientific and technological directions. Such composites have non-linear electric characteristics, which relate to peculiarities of the percolation production of materials doped with conducting particles contacting each other in a non-perfect manner. Nanocarbon particles additive to phase change materials permits one to considerably enhance their thermal conductivity, which in turn offers a possibility for the development of the thermal energy accumulator on the basis of phase change materials. Thereby it seems that the most proper additive is reduced graphene oxide the production procedure of which has been elaborated in detail. Transparent polymer doped with nanocarbon particles can be used in an optical sensor based on the effect of the enhancement of the Raman signal. The waveguide is inserted into a desired region of the organism to be studied, and the information on the chemical content of this region can be obtained from the enhanced scattered Raman spectrum.

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