Influence of solvents on low-temperature reduction--exfoliation of graphene oxide*)

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Abstract: Graphene due to its extraordinary properties and a wide range of potential applications, has aroused a great interest. Although there are many ways to obtain graphene, the existing methods still possess certain disadvantages. Numerous attempts are made to scale up a new and efficient production method of this material on an industrial scale. A very popular method to obtain graphene is a two-step process. It is based on the oxidation of graphite and subsequent reduction to graphene. This article presents a new way of low-temperature reduction of graphene oxide (GO) in presence of various solvents. Indeed, using of appropriate organic solvents in a particular stage of graphene preparation affects the reduction process and the exfoliation of graphene oxide. The possibility to reduce GO in the presence of a disperser opens new paths for the preparation of graphene containing composites.

Keywords: thermal reduction of graphene oxide, low-temperature reduction, organic solvents.

Wpływ rozpuszczalników na niskotemperaturową redukcję-eksfoliację tlenku grafenu

Streszczenie: Grafen cieszy się ogromnym zainteresowaniem ze względu na swoje szczególne właściwości oraz szeroki zakres potencjalnych zastosowań. Znane sposoby otrzymywania grafenu są obarczone pewnymi wadami, co powoduje, że wciąż podejmuje się próby opracowania nowej, skutecznej metody produkcji tego materiału na dużą skalę. Powszechną techniką wytwarzania grafenu jest proces dwuetapowy, polegający na utlenianiu grafitu do jego tlenku, a następnie redukcji do grafenu. W pracy przedstawiono nową metodę niskotemperaturowej redukcji tlenku grafenu (GO) z zastosowaniem różnych rozpuszczalników. Jak wynika z przeprowadzonych badań, użycie odpowiednich rozpuszczalników organicznych na jednym z etapów otrzymywania grafenu pozwala skutecznie zredukować oraz eksfoliować tlenek grafenu. Możliwość redukcji GO w obecności rozpuszczalników odgrywa istotną rolę w procesie otrzymywania kompozytów z udziałem grafenu.

Słowa kluczowe: termiczna redukcja tlenku grafenu, niskotemperaturowa redukcja, rozpuszczalniki organiczne.

Since the publication by A. Geim and K. Novoselov in which they presented method of receiving single-layer graphene, the interest in this material is very large and increases [1]. Due to its extraordinary mechanical, chemical, thermal and electronic properties [2–4], graphene has the potential to be used in a wide range of applications as biosensors, electronic devices, energy conversion and storage, solar cells, composites [5–8]. Despite the researches on graphene lasted for several years, receiving it on a large scale is still very challenging. The existing methods of obtention of graphene are costly, long and environmentally hazardous, that makes the mass production to be seriously envisioned [9, 10]. One of the most promising method of graphene production on a large scale is the reduction of graphene oxide (GO) [11–13]. GO is obtained from the oxidation process of graphite, which can proceed according to methods proposed by Brodie, Staudenmaier or Hummers [14–17]. As a result of strong oxidizing agents action, numerous oxygen-containing functional groups are created: namely, hydroxyl and epoxide are located on the basal plane of GO, while carbonyl, carboxyl are distributed at the edges of GO [18–20].

The reduction of graphene oxide can be conducted in many different ways, depending on applied reducing agents. Among these approaches some deserve atten-

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tion as: chemical reduction, electrochemical reduction, laser irradiation, microwave irradiation, photocatalysis, or solvothermal reduction [21–24]. However, there is one more method of graphene oxide reduction worth distinguishing. It is based on the removal of oxygen-containing functional groups under suitable temperature conditions.

The first method of thermal reduction was described as a rapid heating of GO to 1050 °C under argon atmosphere [25, 26]. Conducting this process at so high temperature involved a huge energy consumption, and, for this reason, it does not seen appropriate for obtaining graphene on a large scale. It has been reported that the thermal reduction can be proceeded at significantly lower temperatures. Indeed, receiving few-layered graphene is possible in the 130–250 °C temperature range if carried out under vacuum [27]. However this pressure requirement makes it difficult to carry out a continuous process for graphene production [28]. The other method of the reduction-exfoliation of GO is based on the conduction of the process under hydrogen atmosphere at about 200 °C [10, 27]. These conditions are difficult to be settled in acceptable safety conditions and that is seriously questions the possibility of a large-scale production of graphene. An interesting alternative to all previously mentioned processes can be the low-temperature reduction-exfoliation of GO by using with aid of various organic solvents. This is precisely this new method we intend to describe in this contribution.

This method enables to obtain in majority few-layer graphene (TRG) well suited to constitute charges in composites materials. The method includes three steps. The first one involves graphite oxidation by the modified Hummers' method which was described previously in reference [29]. In the next step, obtained GO is dispersed in the selected solvents. The ability to form stable dispersion and suitable boiling point are the main criteria for selecting the solvents. The following solvents were chosen: *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl phthalate (DMPh). In first approach, we also tested graphene oxide reduction when dispersed in water. The last step is based on the reduction of the suspended GO at low temperature under ambient atmosphere. Conducted research confirms that the application of appropriate solvent has an impact on the exfoliation and reduction of GO. The possibility to reduce GO in the presence of the dispersing agent has a crucial importance during preparation of composite containing graphene.

EXPERIMENTAL PART

Materials

Graphene oxide (GO) was obtained from a graphite powder with a grain size < 20 μm supplied by Sigma-Aldrich. The other reagents: $NaNO_3$, 98 % H_2SO_4, $KMnO_4$, 30 % H_2O_2, *N,N*-dimethylformamide (DMF), *N,N*-dime-

thylacetamide (DMAc), dimethyl phthalate (DMPh) were purchased in Avantor Performance Materials Poland S.A.

Samples preparation

Graphene oxide was prepared from graphite by a modified Hummers' method. A previously prepared solution of 1 g of $NaNO_3$ in 46 cm³ of H_2SO_4 was added by portions to 2 g of natural graphite powder. The obtained suspension was stirred for 30 min in an ice bath. Then, by portions, 6 g of $KMnO_4$ were added in such a way that the temperature did not exceed 20 °C. The ice bath was removed after 5 min, the contents of the beaker were warmed to 35 °C and stirred for 4 h. Then 90 cm³ of water was poured slowly and stirred again for 15 min. Next, 80 cm³ of warm distilled water (60 °C) and 3 % H_2O_2 aqueous solution were added to reduce the residual $KMnO_4$. Finally, the obtained GO was centrifuged and the product was washed in warm distilled water several times until a pH of 7 was achieved.

The thermal reduction of GO was performed in the presence of various solvents like DMF, DMAc, DMPh, H_2O, whose boiling points are: 153 °C, 168 °C, 282 °C and 100 °C, respectively. GO dispersion was prepared in each of these mentioned solvents. All the samples were sonicated for 1 h and then charged into a metal vessel to be flushed under nitrogen for 5 min. The metal vessel was then quickly inserted into a furnace preheated at 240 °C and kept for one hour to obtain graphene by the thermal reduction-exfoliation of the GO. During the reduction process, the yellow-brown sample gradually yielded a black precipitate.

Methods of testing

The prepared samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) measurements, thermogravimetric analysis (TGA), and electrical conductivity measurements (EC).

– The surface morphology of the samples were examined by using an electron scanning microscope JSM.5500 LV JEOL and the microstructure was observed by using a transmission electron microscope FEI Tecnai™ G2 20 X-TWIN.

– FT-IR analysis measurements were recorded using a Magna-IR 860 spectrophotometer supplied by Thermo-Nicolet, with the following parameters: resolution 4 cm⁻¹; number of scans 32; measurement range 4000–400 cm⁻¹.

– XRD measurements were carried out with a URD 63 Seifert diffractometer. CuK_α radiation (λ = 1.5418 Å) was used at 40 kV and 30 mA. Monochromatization of the beam was obtained by means of a secondary graphite monochromator. A scintillation counter was used as a detector. Investigations were performed in the range of angles 4° to 40° with a step of 0.05°. Each diffraction

profile was corrected of polarization, Lorentz factor, and incoherent scattering.

– The thermal properties of the samples were characterized by thermogravimetry using a Q500 V20.10 Build 36 apparatus. All the measurements were carried out over a temperature range of 30–850 °C with a 10 deg/min heating rate, under nitrogen gas (flow rate 60 cm^3/min).

– The electrical conductivity of pressed graphene pellets was measured at room temperature under constant pressure by placing an upper weight (see Fig. 1). The electrical current was provided by a direct current source unit Keithley 237 and the voltage was measured with an electrometer Keithley 6517A. The conductivity of the samples was calculated from their sheet resistances and their thicknesses. Figure 1 shows a scheme of the experimental setup.
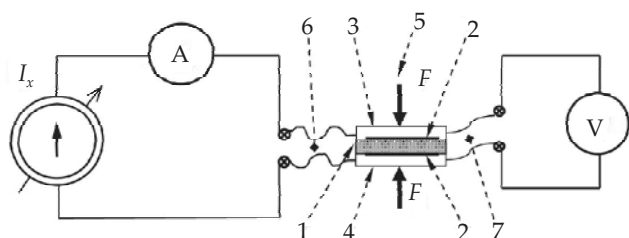
Fig. 1. Scheme of EC measurements: I_x – adjustable current source, A – ammeter, V – voltmeter, 1 – graphene, 2 – metalized surface, 3 – upper electrode, 4 – below electrode, 5 – weight (force F acting on the electrode), 6, 7 – flexible connection of the electrodes

RESULTS AND DISCUSSION

The thermal graphene preparation involves removal of oxygen-containing functional groups by the action of the specific temperature with simultaneous exfoliation of graphene layers [10]. As McAllister explained "exfoliation takes place when the decomposition rate of the epoxy and hydroxyl sites of graphite oxide exceeds the diffusion rate of the evolved gases, thus yielding pressures that exceed the van der Waals forces holding the graphene sheets together" [25]. Depending on the process conditions, ge-

nerated gases during the thermal reduction may produce weakly exothermal reaction. In turn, the different reduction reactions provide graphene of various forms.

In Fig. 2 photographs of received TRG are shown.

This images of samples taken immediately after the reduction confirm that already a partial reduction occurred proved by the color change from brown to black. Reduction of GO dispersed in water was running gently, resulting in receiving graphene in the form of lump. This form of TRG is undesirable because of the difficulties in further processing especially for forming composites. Using a dispersing agent as DMF, DMAc, DMPh, the reduction was accompanied by a mentioned micro-explosion giving a dusty form of graphene. The difference in the course of reduction, resulting in different forms of obtained graphene is certainly due to the difference of boiling points of used solvents. In the reductions of GO dispersed in water we may assume the boiling point of water to be too low respectively to the temperature of the reduction reaction. While conducting the reduction, water probably evaporates rapidly and the other volatile compounds removed from the GO sheets did not generate sufficient pressure to initiate violent reaction mode. Although this sample was reduced and exfoliated the form of lump of the obtained TRG shows that water should not be considered as a convenient solvent for ensuring an effective reduction process.

The SEM images shown in Fig. 3 illustrate the different morphologies of GO before and after the thermal reduction as obtained with various solvents. As it can be seen on GO image, wrinkled and fluffy structure of GO was obtained after oxidation. Partial removal of oxygen-containing functional groups causes the structure of received TRG to be more expanded than the initial structure of GO as consequence of exfoliation process. The TRG obtained from DMPh and H$_2$O shows typical thin crumpled and transparent sheet morphologies of graphene [16, 30]. In case of DMAc and DMF, so-called the comb-like structures are obtained, in which the surface is even much more expanded [9]. This last morphology develops a larger specific surface area which is a real advantage when these samples are used as nanoadditive in polymer composites.
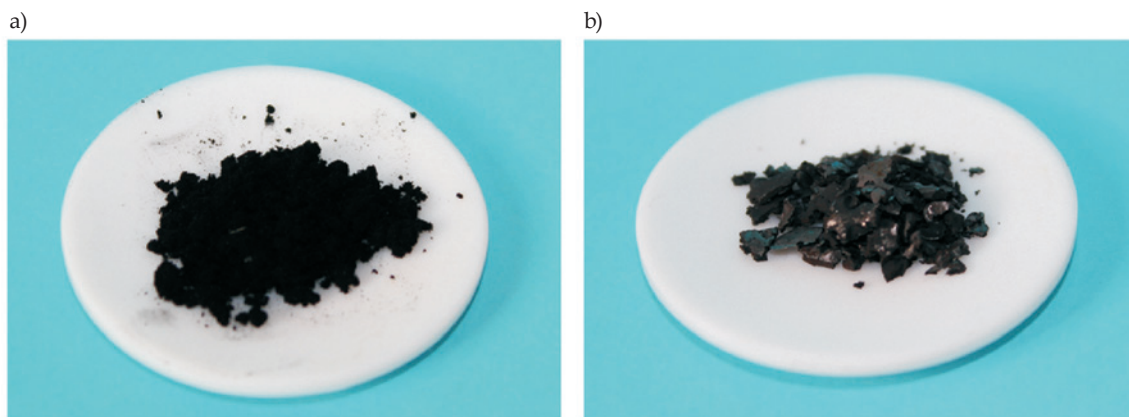
a)

b)

Fig. 2. Digital images showing two different forms of TRG: a) dusty form of TRG obtained from DMF, DMAc, DMPh, b) lump form of TRG obtained from H$_2$O
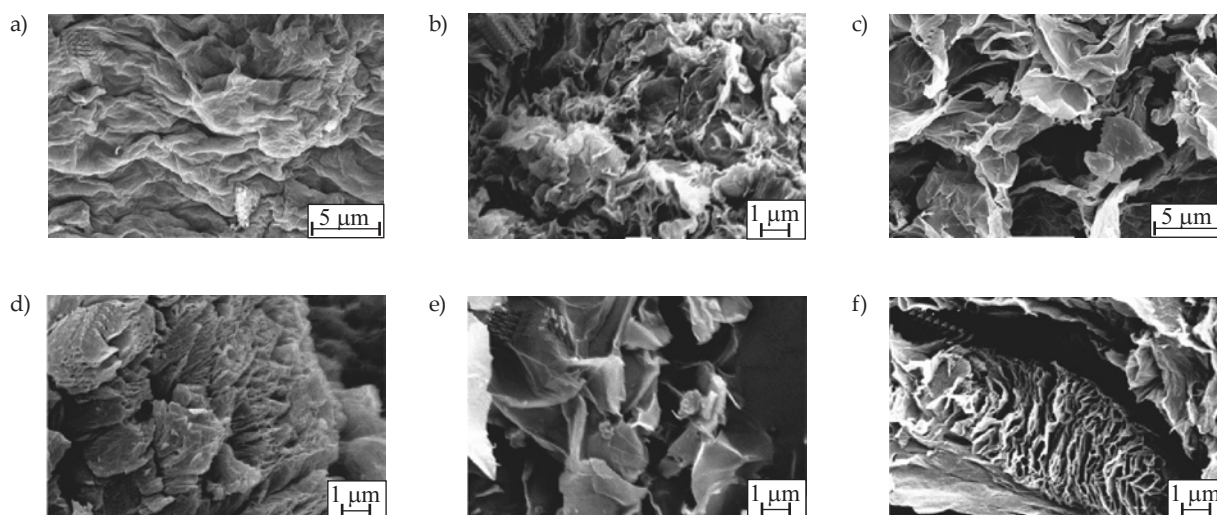
Fig. 3. SEM images of: a, b) GO, and TRG obtained from: c) H$_2$O, d) DMF, e) DMPh, f) DMAc
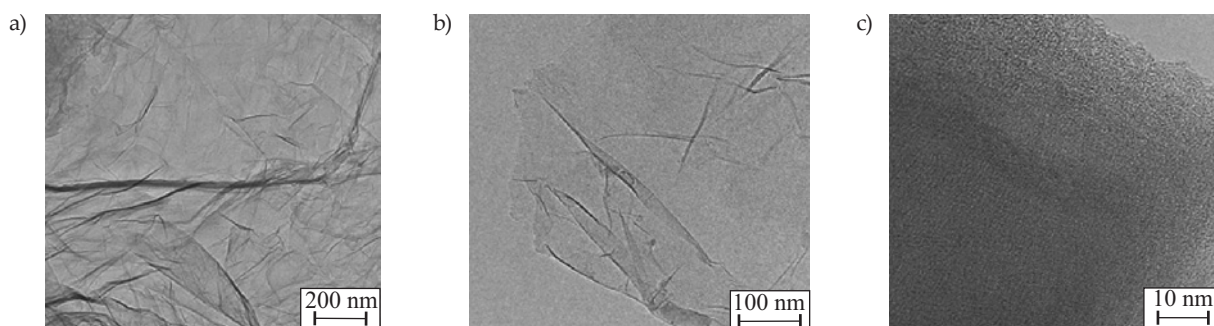

Fig. 4. TEM images of TRG obtained from DMF at different magnification

Interestingly enough, at the scale obtained in TEM images no significant difference between the TRG obtained from various solvents could be really distinguished. As an example the wrinkled transparent structure typical for graphene is showed in Fig. 4 concerning a sample obtained by using DMF.

In Fig. 5 are shown X-ray diffraction profiles of graphite, GO and TRG obtained from various solvents. Graphite diffraction curve is dominated by sharp peak for angle 2θ = 26.5° which is related to parallel structure of the graphene sheets in graphite, corresponding to the (002) plane. In the result of the oxidation in obtained GO this peak is shifted in to direction of smaller diffraction angles. Peak (002) fades out simultaneously appears peak corresponding to the (001) plane. This is related to increase distance between the layers in the consequence of the oxygen-containing functional groups formation. Strong peak on the GO curve as well as secondary order peak visible at angle 2θ = 17.9° indicate very ordered crystalline structure of GO in spite of performed oxidation reaction.

After the thermal reduction for all the TRG samples, the peak at 2θ = 9° disappeared, while a broad peak centered at 2θ = 24° showed up. In each of all of the samples structure of graphite characterized by sharp peak at 2θ = 26° has not been restored. The broad peak occurring in TRG indicates that there are less crystalline regions in comparison to graphite [31, 32], which is the consequence

of the oxidation and reduction reactions. The narrowest peak was noticed for the TRG obtained from DMPh dispersion, which means that the graphene crystallites sizes are the largest from all of the prepared samples.

Table 1 shows the number of layers, roughly estimated by equation (D/d)+1 for GO and TRG obtained from various solvents.

According to the data collected in the Table 1, as it can be observed in each of the samples TRG the average layers number was reduced. The highest layer number was
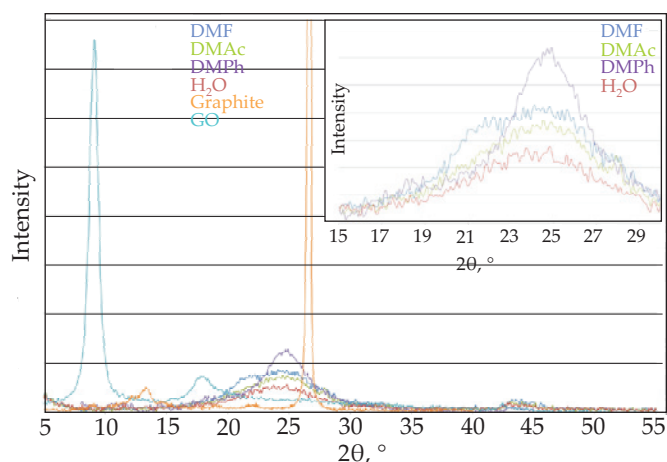

Fig. 5. X-ray diffraction patterns of the pristine graphite, GO and TRG obtained from various solvents

T a b l e 1. XRD and TGA analysis of GO and TRG samples obtained from various solvents

	XRD			TGA		
	D, Å	d, Å	n	1st mass loss % (to 110 °C)	2nd mass loss % (to 360 °C)	3rd mass loss % (to 840 °C)
GO	101.51	9.79	11	7.110	35.90	45.60
TRG/DMF	11.40	3.71	4	1.077	9.35	52.02
TRG/DMAc	12.19	3.68	4	0.838	9.89	42.66
TRG/DMPh	27.25	3.59	8	0.571	9.27	80.19
TRG/H$_2$O	12.49	3.70	4	1.811	13.14	67.18

D – crystallite size, d – interlaminar distance, n – number of layers.

assigned to sample received from DMPh. The boiling point of this compound is the highest, and probably during reduction, DMPh was not able to generate sufficient pressure, which could provide better exfoliation. In the other samples, where the boiling point of the solvent is much lower (below the temperature of the reduction), TRG with 4 layers in average was received.

Concerning IR spectroscopy results, the GO spectrum (Fig. 6) exhibits bands characteristic for oxygen-containing functional groups: C=O stretching vibration at 1748 cm^{-1}, C-OH stretching vibration at 1290 cm^{-1}, C-O-C vibration at 1065 cm^{-1}. We can also notice the wide peak from 2900 cm^{-1} to 3600 cm^{-1}. This peak is related to vibrations modes of O-H bonds in hydroxyl groups [33]. Finally, we will also mention the band at 1622 cm^{-1} corresponding with the aromatic C=C ring stretching.

For the thermal reduced samples the band corresponding to ring vibration is still evident but the hydroxyl groups peak and the characteristic vibration bands for the epoxide groups almost completely disappeared.

It should be mentioned that during the thermal reduction, not all the oxygen-containing functional groups are removed with the same ease. The extent of GO reduction depends not only on the number of oxygen-containing functional groups, but also on the type of these groups. It has been suggested that hydroxyl and epoxide groups

being oxygen-containing functional groups are less stable and removing them is much more easier than removing carbonyl and carboxyl groups [32, 34]. Although the thermal reduction was carried out, the characteristic bands for carbonyl and carboxyl groups at 1748 cm^{-1} and 1290 cm^{-1} are still visible in the spectra shown in Fig. 6.

TGA curves of the graphite oxide and TRG obtained from various solvents are shown in Fig. 7.
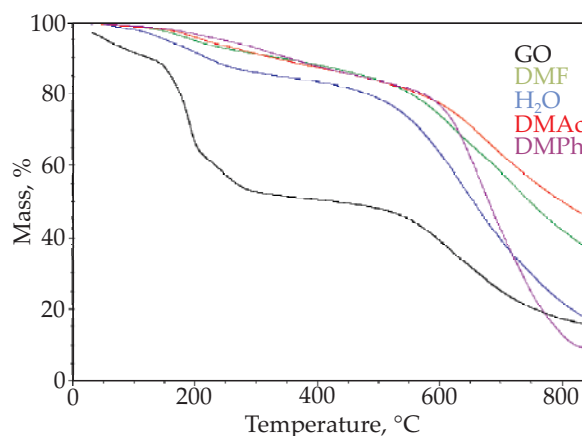
Fig. 7. Thermogravimetric analysis curves of the GO and TRG obtained from various solvents

In case of GO when the temperature is increased, the mass loss occurs in three stages. The first one happens about 100 °C. This phenomenon is related to the release of the remaining intercalated free water molecules between GO sheets. The next stage occurs above 100 °C, where mass reduction is about 35.9 %. This stage is associated with the decomposition of less stable oxygen-containing functional groups on GO sheets. The third decomposition stage results from removal of more stable functional groups and occurs above 360 °C, with a 45.6 % weight loss.

In the case of TRG obtained from various solvents, these three stages are no more so clear. Mass loss about 100 °C does not occur and in the 100–360 °C temperature range the TGA thermal curves are quasi continuous, smooth and with a weight loss of about 9–13 % only (see Table 1). However, the more stable oxygen-containing functional groups release occurs at temperatures aro-
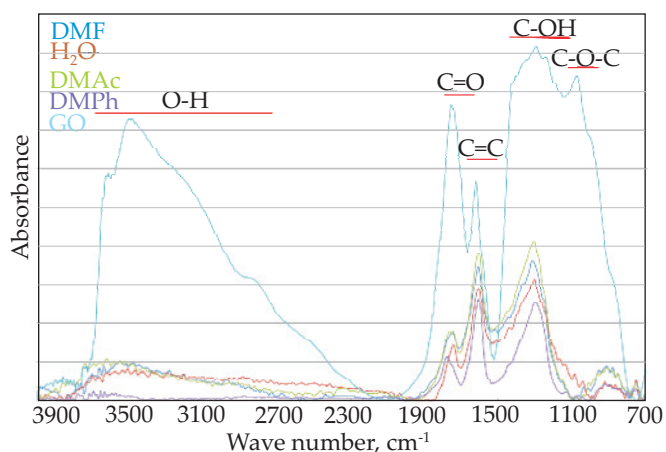
Fig. 6. Fourier transform infrared spectra of the GO and TRG obtained from various solvents
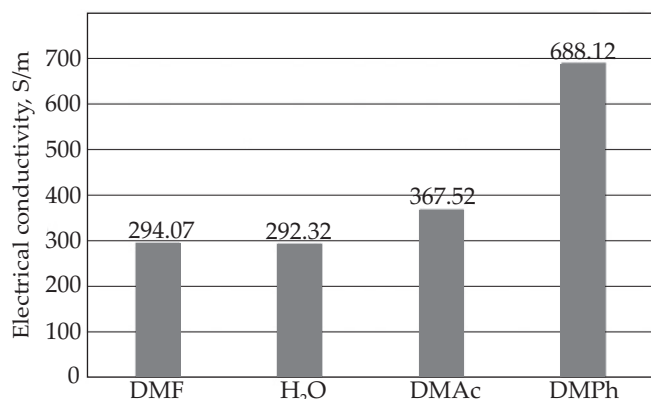
Fig. 8. Electrical conductivity of the TRG obtained from various solvents

und 600 °C. For samples TRG/DMF and TRG/DMAc are observed smaller mass losses in comparison to the other ones proving that these samples contain less oxygen-containing functional groups.

Besides the structure and thermal properties of the resulting graphene the electrical conductivity was measured at room temperature. In Fig. 8 are shown the conductivity values of graphene obtained from various solvents. For TRG obtained from DMF, DMAc, and H_2O electrical conductivities are comparable (290–350 S/m). A significant difference is observed only for TRG/DMPh sample where electrical conductivity is almost twice higher. On the IR spectra of the TRG/DMPh sample no band related to hydroxyl groups (2900–3600 cm^{-1}) is observed. These groups are located mainly on the basal plane of graphene layers [34]. Removal of these groups resulted in restoration of conductive paths effects on growth of the material electric conductivity. Although the highest mass reduction above 360 °C is observed in this sample (Fig. 7) nevertheless above this temperature more stable oxygen functional groups located on the edges of the layers are removed [34]. That is why their presence have less influence on the conductivity of the sample TRG/DMPh.

CONCLUSIONS

The performed research shows that the temperature at which reduction was carried out (240 °C), was sufficient to substantially remove the oxygen functional groups from GO sheets, thereby effectively reducing it. The tested organic solvents (DMF, DMAc, DMPh) used as GO dispersers have an effect on the form of the resulting graphene during low-temperature reduction. Due to its further applications, the most important effect of using suitable solvents is the ability to receive graphene in the form of fine dust with a highly developed specific surface area which could be applicable as a nanoadditive in composites. In addition, the obtained TRGs from various solvents are characterized by different structure. In the case where the boiling point of the solvents were lower than the reduction temperature (DMF, DMAc, H_2O), graphene samples were obtained with an average number of

4 layers. By contrast DMPh with boiling point temperature much higher than the reduction temperature, resulted in TRG having as many as 8 layers. However, this sample, at the same time, was characterized by much higher conductivity, which may be assigned to the smaller content of the less thermally stable oxygen-containing functional groups. The partial presence of oxygen-containing functional groups in the resulting graphene is beneficial and gives the possibility of functionalizing such graphene for the desired properties and uses.

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