Joint Oxidation of Fullerene C_{60} and Graphite

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Abstract--The paper describes preparation of products by joint oxidation of graphite and fullerene C_{60} and it evaluates their properties and structure depending on their mutual weight relations. The characteristics of the products include their ability to form foils, thermal stability (TGA, DSC), identification of functional groups (FT-IR) and morphology (microscopic analysis) of the prepared foils. We have discussed differences in properties of the products and the effect of fullerene quantity on the structure. We have also analyzed effects of the method of foil preparation on its quality, the possibility to combine the foil with nanofibers and the ability to create lamellar fibers by freeze drying.

Keywords--graphite, fullerene C_{60}, foil, nanofibers, oxidation, freeze drying, lamellar fibers

I. INTRODUCTION

Graphene oxide (GO) prepared by oxidation of graphite with strong oxidizing agents is a precursor for chemical preparation of graphene (Makharza et al., 2013). Publications about oxidation of graphite with the objective to produce GO mostly indicate a method developed by specific authors, e.g.: by Hofmann (in the environment of HNO₃, KClO₃), Staudenmaier (in the environment of HNO₃, KClO₃), Tour (in the environment of P₂O₅, KMnO₄), Hummers (in the environment of NaNO₃, KMnO₄). In all the methods the key chemical agent is concentrated sulfuric acid (Chang and Pumera, 2013).

GO is a compound made up of a carbon skeleton with main functional groups, such as carboxyl, carboxyl, epoxy and ether groups and hydroxy- groups. These functional groups enable chemical reactions of GO (Zang et al., 2011) to form covalent bonds with other compounds (e.g. esterification, amidation).

Another option is a GO reaction to form non-covalent bonds (Makharza et. al., 2013). The possible types of the bonds are hydrogen bonds, van der Waals forces, H-π, cation-π, anion-π, π-π, electrostatic forces. These non-covalent bonds are employed in preparation of composite polymers, biopolymers (Yoo, B. M. et. al., 2013) and in use of GO adsorption and absorption properties (Kyzas et. al., 2014; Fakhri et al., 2013; Chabot et. al., 2014). GO suspension can be vacuum filtered to prepare foils that find use in biology, electrical engineering, optics (Russo et. al., 2013) and biomedicine (Shen et. al., 2012).

Graphene can be prepared by a chemical method which consists in reduction of oxidized carbon (functional groups) in GO with various reducing agents (hydrazine, metal hydride, hydrogen, hydrogen iodide) or reducing methods, such as reflux in a polar solvent, microwaves irradiation, electrochemical reduction (Dreyer et. al., 2010).

Another modification of carbon from the realm of nanoparticles are polycyclic carbon compounds called fullerenes; the best known representative is fullerene C_{60} with spherical molecules consisting of 20 hexagonal and 12 pentagonal rings. A fullerene molecule may be subject to nucleophilic and radical reactions (Troshin et. al., 2008).

A principal difference between graphite and diamond is the solubility of C_{60} in non-polar organic solvents and its reactivity. Typical reactions are associated with reconfiguration of sp² to sp³ which reduces strain in the molecule. C_{60} molecules are electropositive and thus they prefer nucleophilic or radical addition on the multiple bond. Fullerene C_{60} can be hydrogenated, alkylated, halogenated, oxidized, polymerized etc.

Equally as with graphene, publications about oxidation of fullerene with the objective to produce C_{60}O or C_{60}(OH)n mostly indicate a method developed by specific authors, e.g. synthesis of polybrominated derivative used as the initial step to produce hydroxy- and oxo-compounds of fullerene and followed by substitution of Br in the C_{60}Br_{24} molecule (Troshin et. al., 2008). Also synthesis has been described of benzene solution C_{60} with a water solution of NaOH with adding of tetrabutyl- ammonium hydroxide (TBHA) catalyst (Li J. et al., 1993). G.C. Alvez modified the method by replacing TBHA with polyethylene-glycol oxygen atmosphere (Alves et.al.,2006). Also successful were oxidations of C_{60} with various types of amine N-oxides induced with ultrasound (Ko W.-B. et. al., 2003). Ultrasonification reduces the reaction time thanks to the generated high pressure and temperature in the reaction environment of the indicated oxidizing agents. An oxidized form of fullerene with high solubility in water has been achieved by reaction with peracetic acid (Zemanová, Klouda, 2012). The advantage of this preparation method consists in the fact that the product, apart from C-O, C-OH, or epoxide bonds, contains no byproducts.
Oxide or epoxide forms of fullerene and graphene can be used as oxygen-transporting materials and as attractive raw materials for preparation of other compounds containing fullerene or graphene. The objective of our work was to evaluate (establish) the mutual impact of graphite on fullerene, and vice versa, in the course of their oxidation. Therefore we performed their joint oxidation using the method most frequently applied for preparation of graphene-oxide from graphite, specifically the method developed by Hummers (Hummers and Offemann, 1958). Apart from the joint oxidation, we also oxidized graphite and fullerene alone for the purposes of comparison. While performing the joint oxidation we also changed the mutual weight ratios of the two components.

The prepared products – mostly in form of foils – were analyzed by FT-IR, TGA-DSC, XDR, their surfaces were inspected by microscopic analysis and foil sections were inspected by SEM. We also analyzed the ability to form combined foils with PCL nanofibers or formation of micro- and nanofibers by freeze drying from water suspension.

II. EXPERIMENTAL PART

2.1 Employed chemicals:

Graphite: PM – very fine crystalline powder graphite, mesh 0.025mm, Supplier: Koh-I-Noor Netolice, Czech Republic

Fullerene C₆₀: 99.5% purity, SES Research, Houston USA

Sulfuric acid, nitric acid, potassium permanganate, hydrogen peroxide: Supplier: Sigma – Aldrich

Polycaprolactone (PCL) was made by Sigma Aldrich, with the molecular weight 45 thousand and its ten percent solution in ethanol was used.

ATR analysis by means of FTIR spectrometry was performed using the spectrometer Brucker Aplha/FT-IR, ART crystal (identified as Platinum Diamond 1 Ref1), software OPUS 6.5, source IR SiC Globar. Number of spectrum scans 24, resolution 4 cm⁻¹, spectrum range 375-4000 cm⁻¹.

Thermal analyses TGA and DSC of the prepared product were performed on STA 1500, Instrument Specialists Incorporated-THASS, analytical scale SUMMIT, SI 234-4, at flow rate 20 ml/min., heating rate 10°C/min., ceramic crucible, diameter 5 mm and height 8 mm, degradation medium: air.

Morphology of the prepared foils was investigated with the microscope Twist Digital Microscope Learning Resource, Inc. USA, foil sections were inspected with SEM Phenom FEI and SEM FEI Quanta 650 FEG (USA).

XDR analysis: Bruker D8 Advance: Measuring geometry 2Q/Q, reflection, divergent orifice 0.32°, 2.3°, detector LynxEye. Measuring conditions – radiation CoKa/Fe filter, 40kV, 40 mA, measuring step 0.0141° 2Q, step time 0.25s, summarization of two measurements, measuring range 3-80° 2Q. The qualitative evaluation used the program Bruker EVA, version 2, the line positions were determined with Bruker Topas, version 4.2.

Mass spectroscope Ultraflextreme (Bruker Daltonics, Billerica, Ma, USA) equipped with 1000 Hz Smartbeam II laser (Nd:YAG, wavelength of the beam 355 nm).

2.2 Methodology

Fullerene C₆₀, graphite and a mixture of graphite and fullerene C₆₀ were oxidized with a mixture of H₂SO₄, KMnO₄ and NaNO₃ according to Hummers and Offemann, 1958. Fullerene, sulfuric acid and sodium nitrate were placed into a reaction flask. The mixture was stirred and cooled to 10°C. Subsequently, potassium permanganate was added in small portions while the mixture was intensely stirred.

After adding the permanganate the reaction mixture was slowly heated to 60°C and stirred at that temperature for 3 hours. Then the mixture was left to stand at the laboratory temperature for three days. The obtained product was filtered off, washed with big quantity of distilled water and hydrogen peroxide and then dried for three days on a Petri dish at 50-60°C to form GO foil or GO-C₆₀ foil or, in case of oxidation of C₆₀ black loose powder.

Weights of samples for the individual experiments I – V are provided below in Table 1.
2.3 Identification of the prepared products

a) Evaluation of IR spectra of the oxidized C$_{60}$ (P-I) and the initial C$_{60}$

The measured IR spectrum of the initial fullerene C$_{60}$ is provided in Fig. 1. The main vibration characteristics for C$_{60}$ (Saeedfar et al., 2013) : 522 cm$^{-1}$, 573 cm$^{-1}$, 1159 cm$^{-1}$, 1426 cm$^{-1}$, are also visible in the spectrum of C$_{60}$-oxi.

In the case of P-I (Fig. 2) additional weak vibrations have been identified in the absorption interval 1556-1644 cm$^{-1}$ (probably C=C, C=O), 1000-1100 cm$^{-1}$ (probably C-O-C epoxy, alkoxy, C-CO-C) and a medium vibration at 702 cm$^{-1}$ (probably a substituted aromatic ring). Based on the characteristic vibrations of the functional groups we can probably exclude presence of the following functional groups on a molecule of C$_{60}$-oxi (P-I): -OH, -COOH, -COOR, -SO$_3$H, -NO$_x$.

b) Thermal stability of oxidized C$_{60}$ (C$_{60}$-oxi, P-I) and initial C$_{60}$

In the measured temperature range, as indicated by TGA and DSC curves (Fig. 3 - 4), there were no thermal effects in either of the tested samples up to ca. 420°C and the weight loss was comparable for both the samples in units of percents (6.1% for C$_{60}$, 8.6% for C$_{60}$-oxi).

In the temperature interval 420-600°C both the samples demonstrated an exothermic reaction, however, the thermal effects were different. The thermal effect in C$_{60}$-oxi was 20-times higher than in the initial C$_{60}$ (1947 kJ/kg for C$_{60}$-oxi in comparison with 180 kJ/kg for C$_{60}$). The weight loss was 56.7% for C$_{60}$-oxi in comparison with 28.8% for C$_{60}$, which is essentially the double.
We have observed a similar reduction of resistance of the carbon skeleton of fullerene on its bromoderivative. After endothermic disruption of the C-Br bond the molecule $C_{60}$ completely (100%) disintegrated at the temperature 420-550°C.

We are fully aware of the fact that this so-called “blank test “ may not completely correspond to the oxidation process in presence of graphite, graphene-oxide, where a carbo-catalytic effect may be involved (Navalon et al., 2014; Su and Loh, 2013).

c) Evaluation of IR spectrums of GO (P-II) and GO-$C_{60}$ (P-III - P-V)

When preparing GO by oxidation methods, FT-IR is usually indicated as a method for identification of basic functional groups. However, in most cases the range of vibrations is indicated for specific functional groups which are expected to be present in GO:

- $3000 – 3700 \text{cm}^{-1}$ ($-\text{COOH}, -\text{OH}, H_2O$)
- $1850 – 1750 \text{cm}^{-1}$ ($-\text{C}=\text{O}$)
- $1650 – 1750 \text{cm}^{-1}$ (carboxy COOH)
- $1500 – 1600 \text{cm}^{-1}$ ($\text{sp}^2 \text{C} = \text{C}$)
- $1280 – 1320 \text{cm}^{-1}$ (epoxide $\text{C} = \text{O}$)

At the same time, the following vibrations may appear:

- $1280 – 1500 \text{cm}^{-1}$: ethers, epoxides, ketones, peroxides,
- $1100 – 1280 \text{cm}^{-1}$: peroxides, ethers, ketones, lactones,
- $900 – 1100 \text{cm}^{-1}$: lactones, peroxides, hydroxyles, 1,3-dioxane,
- $900 – 1100 \text{cm}^{-1}$: lactones, peroxides, hydroxyles, 1,3-dioxane,
- $1720 – 1740 \text{cm}^{-1}$: $\text{C}=\text{O}$ stretching vibration at 3420 $\text{cm}^{-1}$, $\text{C}=\text{O}$ stretching vibration at 1720 – 1740 $\text{cm}^{-1}$.

A comparison of the spectrums obtained for GO (P-II) and GO-$C_{60}$ (P-IV) is shown in Fig. No. 5.

In case of $C_{60}$-oxy the oxidation partly reduced its resistance against temperature exposure. We assume that C-skeleton was partly oxidized (see the IR-spectrum in Fig. 2) and thus its consistence (electron balance) was disturbed which means that subsequent heating may result in defects in its carbon structure e.g. Stone-Wales defect (Kabir et al., 2011).
A dominating feature of the product spectrums (P-II – P-V) is a broad absorption band from 3500 to 2500 cm$^{-1}$ and it belongs to the –OH group. Very intense bands at 2922 cm$^{-1}$ and 2853 cm$^{-1}$ for the product P-III and at 2921 cm$^{-1}$ and 2852 cm$^{-1}$ for the product P-V can be assigned to the vibration –OH of the carboxyl group; it can be confirmed by the vibration at 1412 cm$^{-1}$, which was recorded for those products. They also demonstrated an increased intensity of vibrations of the carbonyl group.

Differences between the spectrums can be found also in the measured absorbance values.

The biggest variance in the vibration values, i.e. 43 cm$^{-1}$, has been found for the stretching vibrations $\nu_c$ (O-C-O), $\nu_{as}$ (O-C-C) and $\nu$ (C-O). In the spectrum range 1400 – 1150 cm$^{-1}$ [ $\nu$ (C-O), $\nu_{as}$ (C-O-C), $\nu$ (C-C), $\delta$ (C-C)] the products demonstrated differences in intensities of the absorption bands and in their identified numbers (see Fig. 5).

The wave number range represents the area with functional groups, such as e.g. secondary and tertiary –OH, esters, ketones, unsaturated esters. Wave numbers of other decisive absorption bands with the assigned functional groups are provided in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Probable assignment [functional group]</th>
<th>Product/wave number, intensity a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_c$ (C-O-C)</td>
<td>GO (P-II) 1068 (s)</td>
</tr>
<tr>
<td>$\nu_{as}$ (C-O-C)</td>
<td>GO-C$_{60}$ (P-III) 979 (m)</td>
</tr>
<tr>
<td>$\nu$ (C-O)</td>
<td>GO-C$_{60}$ (P-IV) 1054 (vs)</td>
</tr>
<tr>
<td>[RCO-OR,-O-, $\equiv$C-O-C, R-CO-C]</td>
<td>GO-C$_{60}$ (P-V) 1073 (vs)</td>
</tr>
<tr>
<td>$\nu$ (C=C)</td>
<td>GO (P-II) 1613 (s)</td>
</tr>
<tr>
<td>$\nu$ (C=O)</td>
<td>GO-C$_{60}$ (P-III) 1620 (m)</td>
</tr>
<tr>
<td>[ &gt; C=C &lt; $\equiv$C=C- elol.$\beta$ diketones]</td>
<td>GO-C$_{60}$ (P-IV) 1607 (vs)</td>
</tr>
<tr>
<td></td>
<td>GO-C$_{60}$ (P-V) 1618 (vs)</td>
</tr>
<tr>
<td>$\nu$ (C=O)</td>
<td>GO (P-II) 1723 (w)</td>
</tr>
<tr>
<td>[O=CR-O-R$_1$-R$_2$, C=O -COOH, $\alpha$, $\beta$, ketones]</td>
<td>GO-C$_{60}$ (P-III) 1741 (s)</td>
</tr>
<tr>
<td></td>
<td>GO-C$_{60}$ (P-IV) 1727 (w)</td>
</tr>
<tr>
<td></td>
<td>GO-C$_{60}$ (P-V) 1734 (m)</td>
</tr>
</tbody>
</table>

a) w- weak, m - medium, s – strong, vs – very strong
Before we conducted those experiments we had had some notion of what we could expect in the course of the reaction and its results. The anticipated functional groups on GO are as follows: carboxyl, carbonyl, epoxide, hydroxyl and partly also lactone and sulfonyle groups. On a fullerene C₆₀ molecule we can expect addition of -SO₃H, -OH, -NO₂, -ONO₂, epoxide groups. A covalent bond (esterification, dehydration, addition) or non-covalent bond (hydrogen bonds, π–π interaction, Van der Waals forces) may develop between groups of those components. Also intercalation of a fullerene molecule may occur between the layers of graphene-oxyde. Even breakage of a fullerene molecule in the conditions of oxidation cannot be excluded.

The quoted work (Trzaskowski et al., 2013) deals with energy possibilities of connection between graphene and C₆₀ in absence of defects on the graphene surface and in presence of such defects. Chemical attachment of C₆₀ to a monolayer of defect-free graphene is not possible for energy reasons. However, in presence of various defects on the C-layer of graphene, such as e.g. formation of 4- and 5-member rings, Stone-Wales defects and other types of defects (e.g. flower defect, okta-, penta-, hepta-disrupted cyclic formations), some spaces may appear or reactive locations may develop and therefore enable potential bonds with fullerene C₆₀.

Non-covalent functionalization (π–π interaction) of partly reduced GO (by hydrazine) was performed in presence of fullerene in xylene solution with ultrasonification. The prepared hybrid was integrated into PEDOT: PSS (poly(3,4-ethylenedioxythiophene): polystyrene sulphonate), (Zhang et al., 2013) to prepare organic thermoelectric material.

Unlike graphene, graphene oxide has some unreduced functional groups (-COOH, -OH, -C=O, epoxy C-O-C). Mutual reaction of GO functional groups with functionalized fullerene has been described, e.g. with groups –OH (Zhang et al., 2009), [2,1 methanofullerene C₆₀] 61-carboxylic acid (Zhang et al., 2011), pyrrolidine fullerene (Liu et al., 2009, Zhang et al., 2009) [6,6]-phenyl – 61 butyric acid methyl ester (Wang et al., 2012). C₆₀ was intercalated as C₆₀(OH)₃ into graphite, which had been initially exposed to reaction with concentrated nitric acid (Kumar et al., 2014), or by direct long-term reaction with C₆₀ solution in toluene (Spyrou et al., 2013). Amine C₆H₂₃NH₂ n=3-8 was intercalated into GO and its intercalate was prepared by its subsequent reaction with C₆₀ solution in toluene. Excess of the amine was eluted with hydrochloric acid (Ishikawa et al., 2010).

The presence of intercalated C₆₀ in GO was identified with a vibration mode (F₁₁₁) at 526 cm⁻¹, but it had a very low intensity in the published spectrums (Ishikawa et al., 2010).

The formation of ester bonds during functionalization of GO by the reaction with s C₆₀(OH)₃ was demonstrated by a change in vibrations of the group –C=O from 1725 cm⁻¹ to 1721 cm⁻¹ for carboxyl (Zhang et al., 2013) and from 1730 cm⁻¹ to 1717 cm⁻¹ for ester (Zhang et al., 2009). However, also a reverse shift to higher –C=O wave numbers was recorded for the formed ester from 1723 cm⁻¹ to 1743 cm⁻¹ for -C=O carboxyl (Kumar et al., 2014).

In case of formation of amide bonds the vibration of the –C=O group shifted to lower values from 1730 cm⁻¹ to 1725 cm⁻¹ (Liu et al., 2009) and the absorbance decreased. For our products we also recorded shifts of vibrations of the –C=O bond always to higher values for GO-C₆₀ products (P-I -V) in comparison to GO. The biggest shift, up to 18 cm⁻¹, was identified for the material prepared by oxidation of graphite: C₆₀ = 1 : 1 (see Table No. 2).

d) Thermal stability of GO (P-II)and GO-C₆₀ (P-IV) foils

Two distinctive peaks were found for samples of GO and GO-C₆₀ foils on the DSC (Fig. 6) curve , which corresponded to exothermic thermal processes. In the case of GO the first exothermic process was accompanied by a significant loss of weight by 43.6% and for GO–C₆₀ it was even bigger, i.e. 51.1 % (see Table No. 3).

In the case of GO the first exothermic process occurred at 190.9°C with the maximum at 225°C and with the thermal effect of 508.4 kJ/kg; in the case of GO-C₆₀ (P-IV) the process started earlier at 182.6°C with the maximum at 205°C and with a smaller thermal effect than that of GO. Values of thermal effects in the individual temperature intervals are provided in Table No. 4. In the case of GO the second exothermic process peaked at 450°C while in the case of GO-C₆₀ (P-IV) it was at 390°C and the detailed shape of the curve was different (compare Fig. a) and Fig. c)). In the case of GO-C₆₀ (P-IV) the weight loss during the second exothermic process was smaller than that of GO, which is different from the first process.

Until the first exothermic process the weight loss was approximately the same for both the foils (ca. 20 %) with a slight endothermic effect, the size of which was bigger for GO (with anticipated dehydronzation). Also the total thermal effect of the decomposition was higher for the GO-C₆₀ foil by 30 % (see Table No. 4).
For P-III and P-V one peak appeared on the DSC curve corresponding to an endothermic process and one distinct peak corresponding to an exothermic process. The exothermic process was accompanied by a substantial decrease of the sample weight. The sample P-III started an exothermic process at 190.2 °C and the peak area on the DSC curve was -345.7 kJ/kg and it reached its maxim at 222.8 °C.

The process is associated with the weight loss of 64.9 %. An equally distinct exothermic process started for the P-V sample at 161.8 °C with the peak area on the DSC curve -385.9 kJ/kg and it was accompanied by the weight loss of 68.6 %. The thermal process reached its maximum at 196.7 °C.
Table 3
Division of the TGA curve into temperature intervals

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Interval No.</th>
<th>Temperature interval (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO foil</td>
<td>1</td>
<td>25.0 – 142.4</td>
<td>11.0</td>
</tr>
<tr>
<td>P-II</td>
<td>2</td>
<td>142.4 – 213.5</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>213.5 – 222.3</td>
<td>43.6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>222.3 – 368.8</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>368.8 – 473.0</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>473.0 – 600.0</td>
<td>6.1</td>
</tr>
<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>25.0 – 50.00</td>
<td>1.7</td>
</tr>
<tr>
<td>P-III</td>
<td>2</td>
<td>50.0 – 131.1</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>131.1 – 185.1</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>185.1 – 214.9</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>214.9 – 231.0</td>
<td>64.9</td>
</tr>
<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>25.0 – 87.1</td>
<td>4.4</td>
</tr>
<tr>
<td>P-IV</td>
<td>2</td>
<td>87.1 – 153.0</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>153.0 – 197.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>197.0 – 205.0</td>
<td>51.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>205.0 – 281.3</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>281.3 – 490.9</td>
<td>18.0</td>
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<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>25.0 – 42.4</td>
<td>1.3</td>
</tr>
<tr>
<td>P-V</td>
<td>2</td>
<td>42.4 – 124.6</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>124.6 – 172.5</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>172.5 – 191.1</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>191.1 – 195.8</td>
<td>68.6</td>
</tr>
</tbody>
</table>

Table 4
Parameters of the thermal processes (DSC)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thermal process No.</th>
<th>Temperature interval (°C)</th>
<th>ΔH (kJ/kg) *</th>
<th>H₂(mW)</th>
<th>ΣΔH (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO foil</td>
<td>1</td>
<td>25.0 – 154.1</td>
<td>874.6</td>
<td>15.8</td>
<td>-910.6</td>
</tr>
<tr>
<td>P-II</td>
<td>2</td>
<td>190.9 – 241.1</td>
<td>-508.4</td>
<td>107.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>356.5 – 492.1</td>
<td>-1277.1</td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>25.0 – 163.1</td>
<td>765.5</td>
<td>8.4</td>
<td>+419.8</td>
</tr>
<tr>
<td>P-III</td>
<td>2</td>
<td>190.2 – 235.0</td>
<td>-345.7</td>
<td>42.6</td>
<td></td>
</tr>
<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>42.0 – 124.2</td>
<td>141.7</td>
<td>6.4</td>
<td>-1204.1</td>
</tr>
<tr>
<td>P-IV</td>
<td>2</td>
<td>182.6 – 221.5</td>
<td>-308.7</td>
<td>71.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>319.7 – 481.6</td>
<td>-1037.1</td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td>GO-C₆₀ foil</td>
<td>1</td>
<td>25.0 – 161.8</td>
<td>1490.0</td>
<td>14.0</td>
<td>+1104.1</td>
</tr>
<tr>
<td>P-V</td>
<td>2</td>
<td>161.8 – 214.8</td>
<td>-385.9</td>
<td>44.7</td>
<td></td>
</tr>
</tbody>
</table>

*ΔH = thermal effect of the process based on DSC curves
(ΔH > 0...endothermic process, ΔH < 0...exothermic process)
The TGA and DSC curves (Fig. No. 6) indicated certain differences in decomposition between P-II and P-IV in comparison to P-III and P-V. The first two types of foils were prepared by filtration of suspension and after washing they were dried at 60°C; the dried foils were thicker than 0.2 mm. The foils made of P-III and P-IV were prepared from suspension thickened by a centrifuge and subsequently dried on a silicone base at 35°C for 3 days. The resulting foils were ca. 0.05 mm thick.

Probably intercalated water caused that the overall decomposition of samples from those foils was endothermic. When we compared thermal effects of the exothermic processes during which all samples demonstrated the biggest weight losses, the thermal effect was the biggest for GO (P-II) , specifically 508 kJ/kg, and for the other samples the values were comparable - for P-III 345 kJ/kg, for P-IV 308 kJ/kg and for P-V 385 kJ/kg, i.e. ca. by 1/3 smaller than for GO.

In the temperature interval up to 250°C the product of oxidation of fullerene alone (P-I) remained essentially stable, see Fig. No. 4. The decomposition occurred only above 450°C with the thermal effect ca. 1947 kJ/kg, which means a major difference in comparison to products of joint oxidation with graphite.

e) XRD analysis and the weight spectrum

One sample of GO-C_{60} (P-IV) foil was analyzed with XRD. The X-ray diffraction pattern (Fig. No. 7) shows extremely strong diffraction for 12.15 °2Q (d=0.845 mm). The diffraction was so much stronger than the other lines that it is necessary to anticipate a strong preferential orientation (see the texture of the sample in Fig. No. 7).

A qualitative analysis identified fullerite lines (fullerene C_{60}), traces of graphite and possibly also fullerene oxide C_{60}O_2.

Mass spectroscopy of the samples P-III and P-V identified an ion with m/z 720 corresponding to the molecule of C_{60}. In both the measuring modes the intensity of the ion m/z 720 was higher for the sample P-III than for the sample P-V. The developed spectrums also contained other fragments [MO]^+ 736 m/z, [MO_3]^+ 768 m/z and [MO - 3C]^+.

In the negative mode of the spectrum m/z peaks of numerous fragments were identified in the product P-V , which can be generally described as [M – xC], where x are even numbers from 2 to 18.
Fig. 7 – XRD spectrum of GO-C$_{60}$ (P-IV), including qualitative identification
2.4 Characteristics of the prepared foils

The products we prepared, except the product of oxidation of fullerene alone, could be prepared in the form of foils (membranes). Published data indicated a number of factors that influenced quality of the foils.

The composition of liquid phase and the concentration (Park et al., 2012) of filtered suspension affect the foil thickness, which is also affected by the speed of filtration and, if the suspension is ultrasonificated, then it is also affected by its duration, temperature and instrument output (Liao et al., 2011).

Properties of the foil can be also influenced by specific treatment, e.g. by washing of the foil with solutions of Cl₂ (Ca, Ba, Mg), when the carbon layers are linked in a plane and across with dialdehyde (Hu et al., 2011), or by impregnation, e.g. with Ti, Ag, Cu₂O (Chen et al., 2011) or by expanding the space between the layers (Zhu et al., 2012) etc.

We have demonstrated that quality of the foils produced from our products was influenced by the method of filtration and drying.
Fast drying at 50-60°C results in point cracking of the foil caused by rapid evaporation of adsorbed water (Fig. 9a). Another factor is the treatment of the initial suspension (without treatment, after ultrasonification, after centrifugation). The best quality foils were obtained when the suspension was repeatedly (at least five times) centrifugated at 2500 rev/min. for 10 minutes and subsequently dried on a silicone foil which has been evaluated as a very suitable base to produce foils up to ca. 50 µm thick. Examples of individual foils with varied ratios of graphite and fullerene are shown in the photographs and microscopic images (see Figs. 9 and 10).

![Examples of the prepared foils after their drying](image)

The microscopic images of foils (Fig. No. 10) indicate that, depending on the ratio of graphite and C_{60} and also depending on the final treatment (vacuum filtration, centrifugation) it is possible to prepare surfaces of foils with a fine structure, with a deeper structure or with a coarse structure with randomly dispersed crystals (P-IV).
GO (P-II)

GO-C_{60} 1:1 (P-III), centrifugation

GO-C_{60}, 2:1 (P-IV)

GO-C_{60}, 3:1 (P-V), centrifugation

Fig. 10 – Fine morphology of selected foils (50x magnification, the line white line = 1 mm, view from the front side of the foil, naturally dispersed light)

The structure of sections prepared from the foils was investigated with scanning electron microscopy. The images have shown a fine, partly deformed lamellar structure (Fig. No. 11). The image shows how the texture of the foils differs depending on the ratio of the oxidized components.
We have also demonstrated that the content of fullerene in the foils affects their specific weight and with the increasing content of fullerene the specific weight decreases as follows:

- GO (P-II) $\rho = 0.975 \text{ g/cm}^3$
- GO-C$_{60}$ (P-V) $\rho = 0.810 \text{ g/cm}^3$
- GO-C$_{60}$ (P-IV) $\rho = 0.228 \text{ g/cm}^3$
- GO-C$_{60}$ (P-III) $\rho = 0.1436 \text{ g/cm}^3$

The prepared products in form of suspensions were combined with PCL nanofibers with the objective to prepare two-layer and multiple-layer foils (sandwich arrangement GO-C$_{60}$PCL-GO-C$_{60}$). After drying the suspension we obtained a foil with the morphology shown in Fig. No. 11. An overview about preparation of the foils, their specific weights and thicknesses is provided in Table 5.

### Table. 5

<table>
<thead>
<tr>
<th>COMBINED FOIL</th>
<th>Sample No.</th>
<th>Composition of the foil layer</th>
<th>Arrangement (of layers)</th>
<th>Note</th>
<th>Thickness of the foil (mm)</th>
<th>Specific weight of the foil (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF-1</td>
<td>GO (P II)</td>
<td>PCL nanofiber</td>
<td>GO-PLC-GO</td>
<td>drying at 30°C</td>
<td>0.175</td>
<td>0.267</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>drying at 75°C</td>
<td>0.060</td>
<td>0.732</td>
</tr>
<tr>
<td>KF-2</td>
<td>GO-C$_{60}$ (P IV)</td>
<td>PCL nanofiber</td>
<td>GO-C$<em>{60}$-PLC-GO-C$</em>{60}$</td>
<td>drying at 30°C</td>
<td>0.253</td>
<td>0.251</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>drying at 75°C</td>
<td>0.227</td>
<td>0.237</td>
</tr>
<tr>
<td>KF-3</td>
<td>GO-C$_{60}$ (P IV)</td>
<td>PCL nanofiber</td>
<td>GO-C$_{60}$-PCL</td>
<td>drying at 30°C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>drying at 55°C</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

PLC nanofibers PCL were prepared by the NANOSPIDER electrostatic spinning technology (developed by the Technical University in Liberec) from a mixture of polymer PCL (15 wt %) + ethanol.

By increasing the temperature used for foil drying above the maximum temperature (65-75°C) of the endothermic process PCL diffused through a layer of GO (P-II) and GO-C$_{60}$ (P-IV), which is visible on sections of the combined foils shown in Fig. No. 12.
The test of thermal stability of the used PCL nanofibers proved an endothermic process (softening) in the temperature range 42.6-89.9°C with the maximum at 60°C and the thermal effect of 123.9 kJ/kg without any weight loss; the weight loss occurred only at temperatures above 350°C (Klouda et al., 2014), see Fig. 12.
GO-C$_{60}$-PCL (where GO-C$_{60}$ 2:1), heated to 30°C

Fig. 11 – Fine morphology of examples of sandwich foils (50x magnification, the white line =1 mm, view from the front side of the foil, natural dispersed light)

GO-PCL-GO 30°C

GO-PCL-GO 75°C

Fig. 12 – Cross sections of sandwich foils with diffused polycaprolactone through GO (P-II) and GO-C$_{60}$ (P-IV), when heated to the temperature of the endothermic process of PCL (magnification 200x, the white line = 1 mm).
Non-covalent attachment occurred also to a foil made of terephthalate, the total thickness of the prepared foil was 97 μm, from which GO-C_{60} (P-IV) made up 82 μm. Apart from the covalent bond between the products and PCL nanofibers, we also tested attachment by ultrasonification between suspensions of P-II and P-IV with PCL nanofibers. Application opportunities for the foils can be found in research of new thermo-optical properties or as materials with an energy potential (solar and thermal cells, cathodic material – Li cells). Other potential use of the foils can be found in medicine and biology, e.g. as an antibacterial material, radio-protective material and adsorption and absorption materials, or also in combination with polymers as a composite material with new properties of the polymer.

2.6 Spinning of GO (P-II.) and GO-C_{60} (P-IV.)

Using a procedure described in the Czech patent (Dvorský, 2011) we performed pilot spinning tests for the products GO (P-II) and GO-C_{60} (P-IV) by controlled freeze drying from their water dispersion.

The results were very satisfactory, mainly for GO-C_{60} (P-IV)(see Fig. 13), which produced yellow-brown opalescent fibers (thick fibrous cotton). A SEM image of a sample of freeze dried fibers is shown in Fig. 14.
The joint oxidation of graphite and fullerene C_{60} was used to produce products for which one can anticipate, based on results of the performed analyses, both intercalation of C_{60} and its partial fixation by a chemical bond to the graphene oxide molecule.

The products, based on the ratio of components in the oxidized mixture and based on the final treatment, can be used to produce foils of diverse morphology. The materials have also demonstrated their ability to form lamellar fibers by freeze drying and lyophilization. We also predict their broad use as adsorption (absorption) materials with new physicochemical properties (electric, optic, etc.).

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REFERENCES


The drying temperature influenced the foil quality – its morphology, we later used a longer drying time at 35°C.