Fullerene C₆₀, graphene-oxide and graphene-oxide foil with fullerene and their bromination

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Abstract: A direct reaction with liquid bromine was used to prepare bromofullerene C₆₀Br₁₄₋₁₈. The brominated derivative reacted with previously prepared graphene-oxide (hereinafter GO), according to a method described by Hummer. The same method was used to oxidize graphite alone. The prepared graphite fullerene foil was brominated with liquid bromine and the graphene-oxide foil was reacted with bromofullerene. FT-IR analysis of all the obtained products was performed and also TGA analysis to investigate particularly their thermal stability. The brominated products demonstrate lower thermal effects when thermally decomposed which is caused by the retarding ability of bromine.

Keywords: Liquid Bromine, Graphene-Oxide Foil, Graphene-Oxide Foil with Fullerene, Brominated Fullerene, Fullerene C₆₀

1. Introduction

Graphite is an allotropic modification of carbon with sp² bonds and made up of layers of mutually interconnected hexagonal rings. The layers are arranged in parallel planes 335 pm apart. Carbon atoms in the adjoining layers are not chemically bonded to each other and they are attached by weak van der Waals forces that make it possible for various atoms or molecules in liquid or gaseous form to get in between the carbon layers. The resulting substances are called intercalation compounds of graphite and their characteristic parameter is the so-called “degree of intercalation“, which indicates the number of carbon layers between two layers of an intercalated substance [1].

Depending on a type of the intercalated substance the graphite plane may be either an acceptor or donor of electrons. Another option is the so-called π-complex created by intercalation of substances of AX_y type, where A is a metal or non-metal with a high valence status, X is an electronegative element and y is a stoichiometric coefficient.

Intercalates of graphite with alkali metals have been

known since 1930s. They are called intercalates of the first degree with the formula C₈M (M=K, Rb, Cs), i.e. they are characterized by a stacking sequence of layers of carbon and alkali metal.

Intercalates of graphite with alkali metals or in combination with other metals have been used in a number of applications as catalysts, e.g. for synthesis of ammonia, synthesis of carbohydrates by hydrogenation of carbon oxides, hydrogenation of olefins, they have sorption properties etc. [1]. Substituents can be chemically bonded to graphite under certain conditions by fluorination or oxidation.

Fluorination of graphite with elemental fluorine at 400-600°C produces a covalent compound called fluorographite CF_x, x = 0.25-1.12, depending on reaction conditions of the fluorination [1].

Oxidation of graphite with strong oxidizing agents (a combination of KMnO₄, KClO₄, NaNO₃ and H₂SO₄) produces graphene oxide (GO), which is a precursor for chemical preparation of graphene [2].

GO is a compound made up of a carbon skeleton with main functional groups, such as carboxyl, carbonyl, epoxy

and ether groups and hydroxy groups. These functional groups enable chemical reactions of GO [3] to form covalent bonds with other compounds (e.g. esterification, amidation).

Another option is a GO reaction to form non-covalent bonds [2]. 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 [4] and in use of adsorption and absorption properties of GO [5-7]. GO suspension can be vacuum filtered to prepare foils that find use in biology, electrical engineering, optics [8] and biomedicine [9].

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 [12].

Another carbon modification from the nanoparticles group are fullerenes and their best known representative is fullerene C₆₀ with a spherical molecule. Fullerene molecule may undergo mostly nucleophilic and radical reactions [10].

Fullerenes are condensed polycyclic carbon substances with a cage structure and with even numbers of carbon atoms arranged preferably into pentagons or hexagons. The most perfect spherical shape has the fullerene C₆₀. Its surface is made up of twenty hexagons and twelve pentagons (similar to a classical sewn soccer ball). The pentagons are made of single covalent bonds and the hexagons are made up of a system of alternating single and double bonds.

The principal difference from graphite and diamond is the solubility of C₆₀ in non-polar organic substances and its reactivity. Its typical reactions are associated with a transformation of arrangement from sp² to sp³ and thus with a reduction of tension in the molecule. The C₆₀ molecule is electropositive which means that it prefers nucleophilic or radical addition on a multiple bond. Fullerene C₆₀ can be used for hydrogenation, alkylation, halogenation, oxidation, polymerization etc.

The contribution describes our “combination experiment”

- bromination of fullerene C₆₀ + subsequent reaction with GO
- bromination of GO-C₆₀ foil and combination of GO with C60

Functional groups of the resulting products were identified with FT-IR. We also determined their thermal stability which is the main topic of this contribution.

2. Experimental Part

Employed chemicals:

Graphite PM – very fine crystalline powder graphite, mesh 0.025mm

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

Sulfuric acid, nitric acid, potassium permanganate, pyridine, tetrahydrofuran, liquid bromine, Supplier: Sigma – Aldrich

Ultrasonification with PS 400A, power output 500 W, thermostat 75°C, frequency 35 Hz

2.1. Measuring Instruments

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

Thermal analyses TGA and DSC of the prepared samples 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 products was determined with SEM Phenom FEI and SEM FEI Quanta 650 FEG (USA).

2.2. Preparation of Graphene-Oxide (Hereinafter GO) by Oxidization of Graphite and Preparation of Graphene-Oxide-C₆₀ (GO-C₆₀) by Oxidization of Graphite and C60 Mixture

Sample weights for the individual experiments:

- 1 g graphite, 0.5 g C₆₀, 2.11 g NaNO₃, 4.6 g KMnO₄, 35 ml H₂SO₄
- 2 g graphite, 2.8 g NaNO₃, 6.5 g KMnO₄, 45 ml H₂SO₄

Graphite and mixtures of graphite + C60 and GO+C60 were oxidized with a mixture of H₂SO₄, KMnO₄ and NaNO₃ according to Hummers and Offerman [11]. Graphite, sulfuric acid and sodium nitrate (in the case of experiments I also fullerene C₆₀) were placed into a flask, the mixture was stirred and cooled to 10°C.

Potassium permanganate was subsequently added into the reaction mixture through a hopper in small doses. The mixture with the permanganate was slowly heated to 60°C and stirred at that temperature for 3 hours. Then it was left to stand for three days at the laboratory temperature.

The obtained products were filtered off, washed with a big quantity of distilled water until negative reaction to sulfate anions and dried for three days on a Petri dish at 50-60°C to form foils of GO and GO-C₆₀.

2.3. Bromination of Fullerene

Fullerene C₆₀ (4 g) was added into liquid bromine 27.5 ml (85.3 g) and the mixture was agitated at the laboratory temperature for 72 hours. The excessive bromine was removed by drying at 75°C for 24 hours until constant weight. The yield was 9.9 g of green-brown substance. According to the weight increase and subsequent elemental analysis, the average composition was C60Br₁₄₋₁₈.

2.4. Modification of Graphene - Oxide (GO) by Reaction with Fullerene Bromo Derivative

GO (0.23 g) from the foil that was cut into tickets sized 2x5 mm was placed into THF (25 ml). The mixture was ultrasonicated for 10 minutes at the laboratory temperature to form suspension of GO in THF. Subsequently, we added

fullerene bromo derivative (0.4 g) and 0.3 ml of pyridine. The suspension was brown. The reaction mixture was ultrasonicated for 10 minutes and then left for 24 hours and intermittently stirred. The suspension was yellow-brown. The solid component was vacuum filtered off and the filter cake was washed with 25 ml HCl (1:3) and 40 ml THF and subsequently dried at 50°C for 2 hours. The process produced 0.6 g of the product.

2.5. Bromination of GO-C₆₀ with Liquid Bromine

The GO-C₆₀ foil (0.15 g) was ultrasonicated in a flask in 10 ml of water solution and then liquid Br₂ (4-5 ml) was added. The reaction mixture was left to stand for 15 days at the laboratory temperature and intermittently stirred. The content of the flask was poured out on a Petri dish and gradually evaporated.

Fig 1. Gradual evaporation of brominated GO-C₆₀ at 35-45°C; reaction of GO-C₆₀ with Br₂ in water environment

3. Results

3.1. Identification of Bromofullerene

There is a number of publications relating to halogen derivatives of fullerenes [13-20] and describing preparation and identification of bromo and chloro derivatives of fullerenes C₆₀. The content of bromine in C₆₀Br_n is defined in the range 2 < n < 24 depending on the reaction conditions (direct contact with bromine, reaction in a solvent, reaction time and temperature, etc.), while the bromine content greater than n=24 is ascribed to an adduct with bromine; also adducts with a solvent have been described in those cases where the bromination is performed in solvents, e.g. in CS₂, CHBr₃, C₆H₄C₁₂ etc. In our case the bromo derivative of fullerene was prepared by direct contact with liquid bromine.

The average composition of the product was determined by elemental analysis and by surface analysis as C₆₀Br₁₄₋₁₈.

a) C₆₀

b) C₆₀Br₁₄₋₁₈

c)

Fig 2. a) Electron image of fullerene, b) bromofullerene c) Energy-dispersive X-ray Spectroscopy (EDAX)

Fig 3. IR spectrum of the bromo derivative of fullerene

FT-IR spectrums were used to identify the following vibrations: 1242 w, 911 w, 844 vs, 773 vs, 749 m, 718 m, 543 m (cm⁻¹) - Fig. 3, the strongest of which is 844 cm⁻¹ and it corresponds to the published data of the strongest vibrations for the bond C-Br. We have also provided the IR spectrum of the initial fullerene C₆₀ for comparison (Fig. 4).

C₆₀Br₂₄ 851 cm⁻¹ [14], C₆₀Br₈ 849 cm⁻¹ [14], C₆₀Br₈ 847 cm⁻¹ [15], C₆₀Br₂₄ 849 cm⁻¹ [15], C₆₀Br₁₄ 842 cm⁻¹ [15], C₆₀Br₈·2Br₂ 720 cm⁻¹, 846 cm⁻¹ [15], C₆₀Br₁₄·Br₂ 842 cm⁻¹ [16], C₆₀Br₂₄·2xBr₂ 846 cm⁻¹ [16].

Fig 4. IR-spectrum of C₆₀

The following data were published on thermal stability of the prepared products of fullerene bromination:

C₆₀Br₂₄ - 2 levels of decomposition at 45°C and 170°C [16]

C₆₀Br₂₄ - at 100°C the beginning, the maximum at 162°C [17-18]

C₆₀Br₂₄ - at 90°C [14]

C₆₀Br₈ - at 70°C – the beginning of decomposition [14]

The pressure of developed gases released by decomposition of C₆₀Br₆ was measured [17] and based on the obtained values the authors assumed gradual decomposition

with partial maximums at 138°C, 175°C and 204°C while in the temperature interval 90-187°C 1 atom of bromine will be released from the cyclopentane circle and cyclopentadienyl radical will operate as an intermediate stage of the decomposition. Then 5 remaining atoms of bromine are expected to be released. The authors anticipate a similar course of decomposition also for C₆₀Br₂₄.

For our C₆₀Br₁₄₋₁₈ the shape of the DSC curves is different in the endothermic process area. In this area we anticipate release of bromine. For the bromo derivative alone the temperature range of the endothermic process is 62°C (126-188 °C) and the shape of the DSC curve is protracted (see Fig. No. 5) which may hide partial maximums and indicate a step-like release of bromine via intermediate products of decomposition, e.g. C₆₀Br₈.

The endothermic effect is 326.8 kJ/kg with the weight loss of 57%, the exothermic effect occurs in the temperature interval 418 – 504 with ΔH 4233 kJ/kg with the weight loss of 32%. A 10% weight loss of the sample occurred between the endothermic and exothermic processes (see Fig. 5).

Fig 5. Thermal analysis of the initial bromo derivative C₆₀Br₁₄₋₁₈ (degradation medium: air, air flow rate 20 ml/min, temperature 25-600° C, heating rate 10°/min, sample weight 9.3 mg).

Fig 6. IR spectrum of fullerene bromo-derivative after heating to 250 °C

In order to confirm the main source of the weight loss during the endothermic process we heated the sample to 250°C and analyzed it with FT-IR spectroscopy. The obtained spectrum in Fig. 6 corresponds to the IR spectrum of the initial fullerene (compare Figures 4 and 6). This confirms our assumption that all bromine is released up to the temperature of 250°C.

3.2. Modification of Graphene-Oxide by Reaction with Fullerene Bromo Derivative

The measured spectrum of the obtained product is shown in Fig. 7. Spectrums of the initial substances are provided in Fig. 8 and Fig. 3 for comparison.

Fig 7. IR spectrum of a product of the reaction of GO with fullerene bromo derivative

Dominant vibrations:

For GO the skeleton vibration is at 1613 cm^{-1} and the vibration of C=C bonds in GO-C₆₀Br is at 1610 cm^{-1} and it is no more dominant.

There are new dominant vibrations at 1091 cm^{-1} and 1045

cm^{-1} that include bond vibrations of a whole range of possibilities from epoxides, hydroxyles, C-O-C (for GO the value was 1068 cm^{-1}).

A similar range of the potential groups for GO is covered by vibrations at 1068 cm^{-1} and 979 cm^{-1} . Vibrations characterizing the groups C=O for GOC₆₀Br_x shifted towards the higher value 1745 cm^{-1} in comparison to 1727 cm^{-1} for GO.

Fig 8. IR spectrum of the initial GO

New vibrations characterizing C-Br bonds were measured as dominant for GOC₆₀Br_x at 741 cm^{-1} and 672 cm^{-1} (the value of 845 cm^{-1} for C-Br in the initial bromo derivative, which was dominant in it, was also found for the same bond in GOC₆₀Br_x with a lower absorbance value – 839 cm^{-1}). The broad absorbance band 2400-3500 cm^{-1} was divided, which probably corresponds to the O-H valence vibration of new carboxyl functional groups. New vibrations, which had not been identified for GO and bromofullerene, appeared for the product at 1534 cm^{-1} , 1478 cm^{-1} and 1417 cm^{-1} .

3.3. Thermal Tests of the Products

Fig 9. Thermal analysis of a product of GO reaction with fullerene bromo derivative (degradation medium: air; air flow rate 20ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 8.6 mg).

Fig 10. Thermal analysis of GO foil (degradation medium: air, air flow rate 20 ml/min, temperature 25-600° C, heating rate 10°/min, sample weight 10.0 mg).

The comparison of thermal stabilities of the initial GO, the used fullerene bromo derivative and the prepared product has shown that the first exothermic process starts for GO at 190.9°C with the maximum at 225°C and with the thermal effect of 508.4 kJ/kg. For the prepared product the first exothermic process starts at a temperature by 40°C lower, with the maximum at 64°C and with a lower thermal effect, specifically 385.9 kJ/kg – see Fig. 9, 10 and Tab. 1,2). The thermal effect of the second exothermic process is also lower and it is approximately one half of that of GO. The weight loss during the first exothermic process of GO is more than 20% lower than that of the prepared product. In case of weight loss during the second process the situation is reverse. The total thermal effect of the decomposing reaction is significantly higher than in the case of the initial GO. For the fullerene bromo derivative alone the decomposition (debromination) occurs in the temperature interval 124-184°C with an endothermic effect (161 kJ/kg) and with a significant weight loss of 47.6%. This explains the lower thermal effect during the first exothermic process of the

prepared product and the higher weight loss than for GO alone. Further decomposition of the initial fullerene bromo derivative occurs in the temperature interval 459-569°C, which is ca. by 60°C higher than the temperature of the second exothermic process of the prepared product.

Tab 1. Division of the TGA curve into temperature intervals

Sample No.	Thermal process No.	Temperature range (°C)	Weight loss (%)
GO-C ₆₀ Br _x (x=14-18)	1	25.0 – 169.4	10.1
	2	169.4 – 178.0	66.3
	3	178.0 – 268.3	5.1
	4	268.3 – 362.0	13.0
	5	362.0 – 458.7	1.4
	6	458.7 – 600.0	3.8
GO foil	1	25.0 – 142.4	11.0
	2	142.4 – 213.5	8.8
	3	213.5 – 222.3	43.6
	4	222.3 – 368.8	2.8
	5	368.8 – 473.0	18.1
	6	473.0 – 600.0	6.1

Tab 2. Parameters of the ongoing thermal processes (DSC)

Sample No.	Thermal process No.	Temperature range (°C)	ΔH (kJ/kg) *	H _n (mW)	ΣΔH (kJ/kg)
GO-C ₆₀ Br _x (x=14-18)	1	25.0 – 126.5	517.1	8.2	
	2	150.5 – 195.4	-385.9	75.5	-517.1
	3	366.9 – 465.8	-648.9	22.5	
GO foil	1	25.0 – 154.1	874.6	15.8	
	2	190.9 – 241.1	-508.4	107.4	-910.6
	3	356.5 – 492.1	-1277.1	31.0	

*ΔH = thermal effect of the process based on the DSC curves
(ΔH > 0...endothermic process, ΔH < 0...exothermic process)

Fig 11. Shows the complex surface structure of the prepared product GO-C₆₀Br_x (x=14-18).

3.4. Reaction of GO-C₆₀ Foil with Liquid Bromine

3.4.1. Evaluation of the IR Spectrum of GO-C₆₀ Foil Brominated with Liquid Bromine

The IR spectrums of GO-C₆₀ and its brominated product (Fig. 12 and 13) demonstrate the following general differences: wave number shifts, changes in values of

absorbances and changes in intensities of vibrations with common assignment for both the substances, such as e.g. changes of mutual intensities of vibrations of the –C=C– bond in respect to C–O–C (from 1:1 for GO-C₆₀ to 1:3 for [GO-C₆₀]Br_x), increase in vibration intensities of the bonds –C=O or –COOH compared to –C=C– (3x for [GO-C₆₀]–Br_x).

The main shift in the vibrations occurred for the broad band characterizing bond vibrations of the –OH group, where the maximum of absorbance for GO-C₆₀ is at the value lower

by ca. 200 cm^{-1} . The vibration of the C-O-C group for GO- C_{60} has the wavenumber higher by 24 cm^{-1} .

A significant difference of the IR spectrum of the brominated derivative is the presence of vibrations at 871 cm^{-1} and 571 cm^{-1} , to which we have assigned the valence vibration of the C-Br bond, and the presence of a new strong vibration at 1153 cm^{-1} , which can be assigned both to the

deformation vibration of the C-Br bond and to deformation of C-CO-C and valence of C-O. Another difference consists in the fact that the spectrum of the bromo-product practically lacks any absorbance in the interval $1220\text{--}1380\text{ cm}^{-1}$, which had been present as medium strong in the spectrum of the initial GO- C_{60} and which we had assigned to the epoxy groups, deformation of -OH and etheric groups.

Fig 11. Electron image of a product of GO reaction with $\text{C}_{60}\text{Br}_{14-18}$, different scales.

Fig 12. IR-spectrum of the initial GO- C_{60}

Fig 13. IR-spectrum of $[\text{GO}-\text{C}_{60}]\text{-Br}_x$

3.5. Thermal Stability of the GO- C_{60} Foil Brominated with Liquid Bromine

For the brominated GO- C_{60} product the thermal analysis has demonstrated one endothermic process and two exothermic processes (Fig. 14). Unlike the TGA analysis of the GO- C_{60} foil, the brominated product $\text{C}_{60}\text{Br}_{14-18}$, when thermally exposed, does not manifest such a sharp weight loss as the GO- C_{60} foil. In the temperature interval $213\text{--}222^\circ\text{C}$ the weight loss was 44% (Fig. 15) and for $\text{C}_{60}\text{Br}_{14-18}$ in the temperature interval $126\text{--}188^\circ\text{C}$ the weight loss was 56% (Fig. 5). Therefore, with a certain approximation, we can assume a gradual loss of weight (Tab. 3). The endothermic process in the product brominated with liquid bromine comes earlier than in the case of $\text{C}_{60}\text{Br}_{14-18}$ and its thermal effect is ca. 4 times bigger. The second exothermic process starts at a higher temperature in comparison with GO- C_{60} , while the first exothermic process occurs at a lower temperature.

Also interesting is the overall result of the thermal processes in the course of thermal decomposition, which is significantly smaller for brominated GO- C_{60} foil (301 kJ/kg) than for the initial GO- C_{60} foil (1204 kJ/kg). For $\text{C}_{60}\text{Br}_{14-18}$ it is up to 3906 kJ/kg . In this case an important role in the total thermal effect is probably played by the considerable size of the endothermic effect of the brominated foil.

Bromine water with oxidizing effects may cause an increase in the number of carbonyl or carboxyl groups, due to splitting of the C-O-C bond. This can be concluded from the IR spectrum (absence of vibrations in the interval $1220\text{--}1380\text{ cm}^{-1}$). Moreover, it is not possible to exclude addition of OH^- Br^+ on the molecule or substitution of H^+ with bromine in the carboxyl. Based on a comparison with the size of the

endothermic effect in C₆₀Br₁₄₋₁₈ we anticipate various types of bromine bonds to the molecule. The size of the

endothermic effect may also result in formation of an adduct of bromine and the molecule.

Fig 14. Thermal analysis [GO- C₆₀]-Br (degradation medium: air; air flow rate 20 ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 10.05 mg).

Fig 15. Thermal analysis foil GO-C₆₀ (degradation medium: air; air flow rate 20ml/min, temperature 25-600°C, heating rate 10°/min, sample weight 10.0 mg).

Tab 3. Division of the TGA curve into temperature intervals ^x

Sample No.	Interval No.	Temperature range (°C)	Weight loss (%)
GO-C ₆₀ -Br	1	25.0 – 56.7	2.7
	2	56.7 – 114.0	20.3
	3	114.0 – 165.1	20.3
	4	165.1 – 259.4	12.6
	5	259.4 – 313.1	14.8
	6	313.1 – 504.1	12.6
	7	504.1 – 546.6	14.3
	8	546.6 – 600.0	0.9
GO-C ₆₀ foil	1	25.0 – 87.1	4.4
	2	87.1 – 153.0	8.2
	3	153.0 – 197.0	8.0
	4	197.0 – 205.0	51.1
	5	205.0 – 281.3	10.8
	6	281.3 – 490.9	18.0

^x the indicated intersections of tangents to the respective bends of the TGA curve

Tab 4. Parameters of the ongoing thermal processes (DSC)

Sample No.	Thermal effect No.	Temperature range (°C)	ΔH (kJ/kg) *	H _n (mW)	ΣΔH (kJ/kg)
GO-C ₆₀ -Br	1	25.0 – 131.9	1288.6	32.0	
	2	131.9 – 171.9	-180.1	21.8	-301.3
	3	253.3 – 322.8	81.5	2.0	
	4	478.6 – 557.3	-1490.7	67.2	
GO-C ₆₀ foil	1	42.0 – 124.2	141.7	6.4	
	2	182.6 – 221.5	-308.7	71.1	-1204.1
	3	319.7 – 481.6	-1037.1	28.1	

ΔH = thermal effect of the process based on DSC curves (ΔH > 0...endothermic process, ΔH < 0...exothermic process)

H_n = height of the peak of a thermal process on the DSC curve in an absolute value related to the point corresponding to the beginning of the thermal process

4. Discussion

Tens and hundreds of products (substances) have been described which were prepared by functionalization of graphene or graphene-oxide while forming both covalent and non-covalent bonds [21]. These products have different physicochemical properties. In the case of graphene the reactions proceed via a reactive intermediate, such as radical, carbene, aryne, nitrene or newly bonded substances [22]. Functional groups, such as $-OH$, $-COOH$, epoxy are used for the reaction of graphene-oxide. A classical example is a reaction with amines [23] when the group $-COOH$ converts into $COCl$ and the latter reacts readily with an amino group of the new substituent.

Graphene-oxide can be also functionalized with non-covalent bonds (van der Waals forces, hydrogen bonds, π - π interaction). As an example, we can provide its reaction with polymers, surface active substances, biomolecules etc. [24].

In the case of graphene and fullerene a product has been described with an interconnection based on π - π interaction. The product has interesting thermoelectric properties [25]. The interconnection of fullerene and GO with a covalent bond has been also described, specifically the reaction of substituted fullerene ($-OH$, $-NH_2$), fullerene pyrrolidine, 1,2 methano-fullerene – 61 – carboxyl acid [26-28] with active GO groups.

5. Conclusion

A direct reaction with liquid bromine was used to prepare bromofullerene $C_{60}Br_{14-18}$. Further, graphene-oxide (GO) was prepared and reacted with the brominated fullerene. Results of the performed analyses have not positively shown whether the reaction of GO with $C_{60}Br_{14-18}$ lead to functionalization of GO with covalent or non-covalent bonds. We assume potential partial esterification, also thanks to the alkaline environment. The shape of the thermal curve of a product of GO reaction with $C_{60}Br_{14-18}$ is similar to that of GO and $GO-C_{60}$.

Another alternative was direct bromination of a $GO-C_{60}$ mixture or foil created from the product. It was accompanied by partial oxidization, i.e. oxidization splitting of C-O-C bonds, epoxide bonds and bromination. The thermal decomposition of the product proceeded without external weight losses (unlike in the case of GO and initial $GO-C_{60}$).

In the process of thermal decomposition the prepared brominated GO and $GO-C_{60}$ demonstrated lower thermal effects, which was caused by retardant ability of bromine.

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