

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 bromo fullerene 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 bromo fullerene. FTIR 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.

Index terms— liquid bromine, fullerene C₆₀, graphene-oxide foil, graphene-oxide foil with fullerene, brominated fullerene.

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 "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 fluoro-graphite 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).

45 Another option is a GO reaction to form noncovalent bonds [2]. The possible types of the bonds are hydrogen
46 bonds, van der Waals forces, H-?, cation-?, anion-?, ?-?, electrostatic forces. These non-covalent bonds are
47 employed in preparation of composite polymers, biopolymers [4] and in use of adsorption and absorption properties
48 of GO [5][6][7]. GO suspension can be vacuum filtered to prepare foils that find use in biology, electrical
49 engineering, optics [8] and biomedicine [9].

50 Graphene can be prepared by a chemical method which consists in reduction of oxidized carbon (functional
51 groups) in GO with various reducing agents (hydrazine, metal hydride, hydrogen, hydrogen iodide) or reducing
52 methods, such as reflux in a polar solvent, microwaves irradiation, electrochemical reduction [12].

53 Another carbon modification from the nano particles group are fullerene and their best known representative
54 is fullerene C 60 with a spherical molecule. Fullerene molecule may undergo mostly nucleophilic and radical
55 reactions [10].

56 Fullerenes are condensed polycyclic carbon substances with a cage structure and with even numbers of carbon
57 atoms arranged preferably into 12 hexagons and 20 pentagons (similar to a classical soccer ball).
58 The pentagons are made of single covalent bonds and the hexagons are made up of a system of alternating single
59 and double bonds.

60 The principal difference from graphite and diamond is the solubility of C 60 in non-polar organic substances
61 and its reactivity. Its typical reactions are associated with a transformation of arrangement from sp² to sp³ and
62 thus with a reduction of tension in the molecule. The C 60 molecule is electropositive which means that it prefers
63 nucleophilic or radical addition on a multiple bond. Fullerene C 60 can be used for hydrogenation, alkylation,
64 halogenation, oxidation, polymerization etc.

65 The contribution describes our "combination experiment"

66 ? Bromination of fullerene C 60 + subsequent reaction with GO

67 ? Bromination of GO-C 60 foil and combination of GO with C 60 Functional groups of the resulting products
68 were identified with FT-IR. We also determined their thermal stability which is the main topic of this contribution.

69 2 II.

70 Experimental Part [11]. Graphite, sulfuric acid and sodium nitrate (in the case of experiments I also fullerene C60)
71 were placed into a flask, the mixture was stirred and cooled to 10°C.

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

75 The obtained products were filtered off, washed with a big quantity of distilled water until negative reaction
76 to sulfate anions and dried for three days on a Petri dish at 50-60°C to form foils of GO and GO-C 60 . c)
77 Bromination of Fullerene Fullerene C 60 (4 g) was added into liquid bromine 27.5 ml (85.3 g) and the mixture was
78 agitated at the laboratory temperature for 72 hours. The excessive bromine was removed by drying at 75°C for
79 24 hours until constant weight. The yield was 9.9 g of green-brown substance. According to the weight increase
80 and subsequent elemental analysis, the average composition was C 60 Br 14-18 .

81 3 d) Modification of Graphene -Oxide (GO) by Reaction

82 with Fullerene Bromo Derivative GO (0.23 g) from the foil that was cut into tickets sized 2x5 mm was placed into
83 THF (25 ml). The mixture was ultrasonicated for 10 minutes at the laboratory temperature to form suspension
84 of GO in THF. Subsequently, we added fullerene bromo derivative (0.4 g) and 0.3 ml of pyridine. The suspension
85 was brown. The reaction mixture was ultrasonicated for 10 minutes and then left for 24 hours and intermittently
86 stirred. The suspension was yellow-brown. The solid component was vacuum filtered off and the filter cake was
87 washed with 25 ml HCl (1:3) and 40 ml THF and subsequently dried at 50°C for 2 hours. The process produced
88 0.6 g of the product.

89 4 e) Bromination of GO-C 60 with Liquid Bromine

90 The GO-C 60 foil (0.15 g) was ultrasonicated in a flask in 10 ml of water solution and then liquid Br₂ (4-5

91 5 Results

92 6 a) Identification of Bromo fullerene

93 There is a number of publications relating to halogen derivatives of fullerenes [13][14][15] [16][17][18][19][20]
94 and describing preparation and identification of bromo and chloro derivatives of fullerenes C 60 . The content of
95 bromine in C 60 Br n is defined in the range 2 < n < 24 depending on the reaction conditions (direct contact
96 with bromine, reaction in a solvent, reaction time and temperature, etc.), while the bromine content greater than
97 n=24 is ascribed to an adduct with bromine; also adducts with a solvent have been described in those cases where
98 the bromination is performed in solvents, e.g. in CS₂, CHBr₃, C₆H₄Cl₂ etc. In our case the bromo derivative
99 of fullerene was prepared by direct contact with liquid bromine. The average composition of the product was
100 determined by elemental analysis and by surface analysis (C 60 Br 14-18 ml) was added. There action mixture
101 was left to stand 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. ??, 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 Br₂₄ for comparison (Fig. 4). C₆₀ Br₂₄ 851 cm⁻¹ [14], C₆₀ Br₈ 849 cm⁻¹ [14], C₆₀ Br₈ 847 cm⁻¹ [15], C₆₀ Br₂₄ 849 cm⁻¹ [15], C₆₀ Br₁₄₈₄₂ cm⁻¹ C₆₀ Br₂₄ -at 100°C the beginning, the maximum at 162°C [17][18] C₆₀ Br₂₄ -at 90°C [14] C₆₀ Br₈ -at 70°C -the beginning of decomposition [14] The pressure of developed gases released by decomposition of C₆₀ Br₆ 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 ring 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 C₆₀ Br₂₄.

For our C₆₀ Br₁₄₋₁₈ the shape of the DSC curves is different in the end other mic process area. In this area we anticipate release of bromine. For the bromo derivative alone the temperature range of the end other mic process is 62°C (126-188 °C) and the shape of the DSC curve is protracted (see Fig. 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 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). In order to confirm the main source of the weight loss during the end other mic process we heated the sample to 250°C and analyzed it with FT-IR spectroscopy. The obtained spectrum in Fig. ?? 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.

7 b) Modification of Graphene-Oxide by Reaction with

Fullerene Bromo Derivative

The measured spectrum of the obtained product is shown in Fig. 7. Spectra of the initial substances are provided in Fig. ?? and Fig. ?? for comparison. For GO the skeleton vibration is at 1613 cm⁻¹ and the vibration of C=C bonds in GO-C₆₀ 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, hydroxyls, 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 GO-C₆₀ Br_x shifted towards the higher value 1745 cm⁻¹ in comparison to 1727 cm⁻¹ for GO. Fig. ?? : IR spectrum of the initial GO. New vibrations characterizing C-Br bonds were measured as dominant for GO-C₆₀ Br_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 GO-C₆₀ Br_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 bromo fullerene, appeared for the product at 1534 cm⁻¹, 1478 cm⁻¹ and 1417 cm⁻¹. 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. ??, 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. The IR spectra of GO-C₆₀ and its brominated product (Fig. 12) show 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-C₆₀ has the wave number 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 1220-1380 cm⁻¹, which had been present as medium strong in the spectrum of the initial GO-C₆₀ and which we had assigned to the epoxy groups, deformation of -OH and etheric groups. For the brominated GO-C₆₀ product the thermal analysis has demonstrated one endothermic process and two exothermic processes (Fig. 14). Unlike the TGA analysis of the GO-C₆₀ foil, the brominated product C₆₀ Br₁₄₋₁₈, when thermally exposed, does not manifest such a sharp weight loss as the GO-C₆₀ foil. In the temperature interval 213 -222°C the weight loss was 44% (Fig. 15) and for C₆₀ Br₁₄₋₁₈ in the temperature interval 126 -188°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 C 60 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 C 60 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 vibration in the interval 1220-1380 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 C 60 Br 14-18 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.

8 Interval

No.

9 Temperature range (°C)

Weight loss (%) H fl = 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 IV.

10 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 a new connection 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 there action of substituted fullerene (-OH, -NH₂), fullerene pyrrolidine, 1, 2 methanofullerene-61-carboxyl acid [26][27][28] with active GO groups.

V.

11 Conclusion

A direct reaction with liquid bromine was used to prepare bromo fullerene 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 retardability of bromine.

12 H

Table ?? : Division of the TGA curve into temperature intervals x ^{1 2}

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1

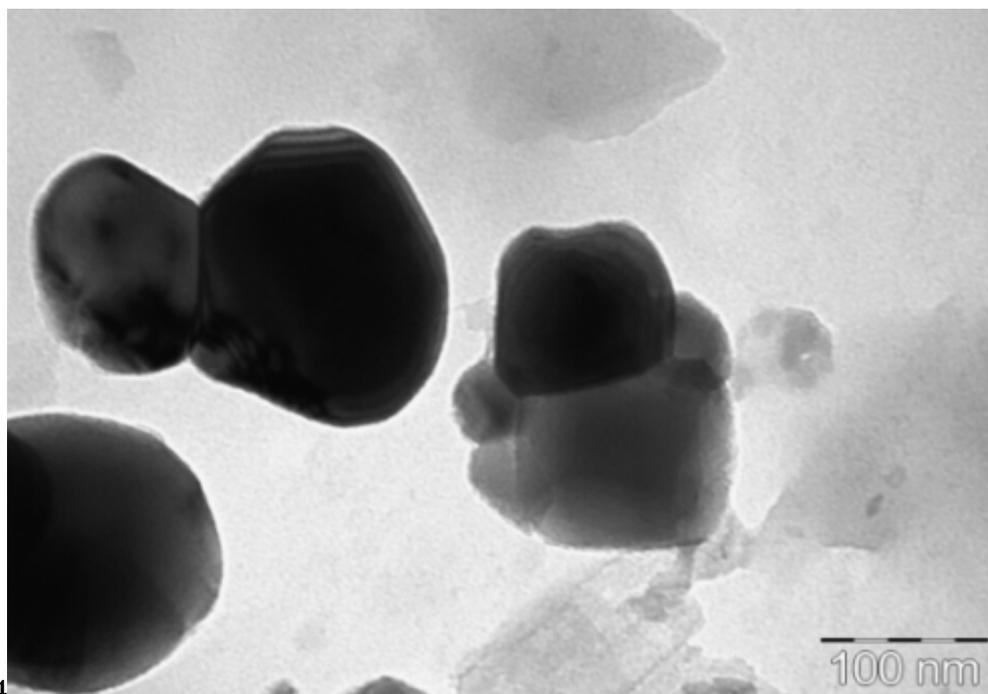
Figure 1: Fig. 1 :



Figure 2:



Figure 3:



4

Figure 4: Fig. 4 :

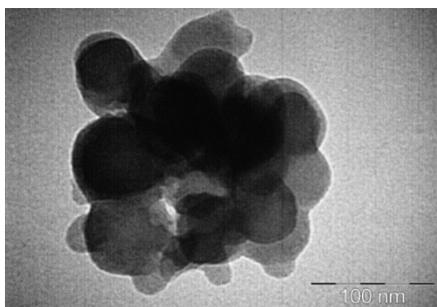


Figure 5:

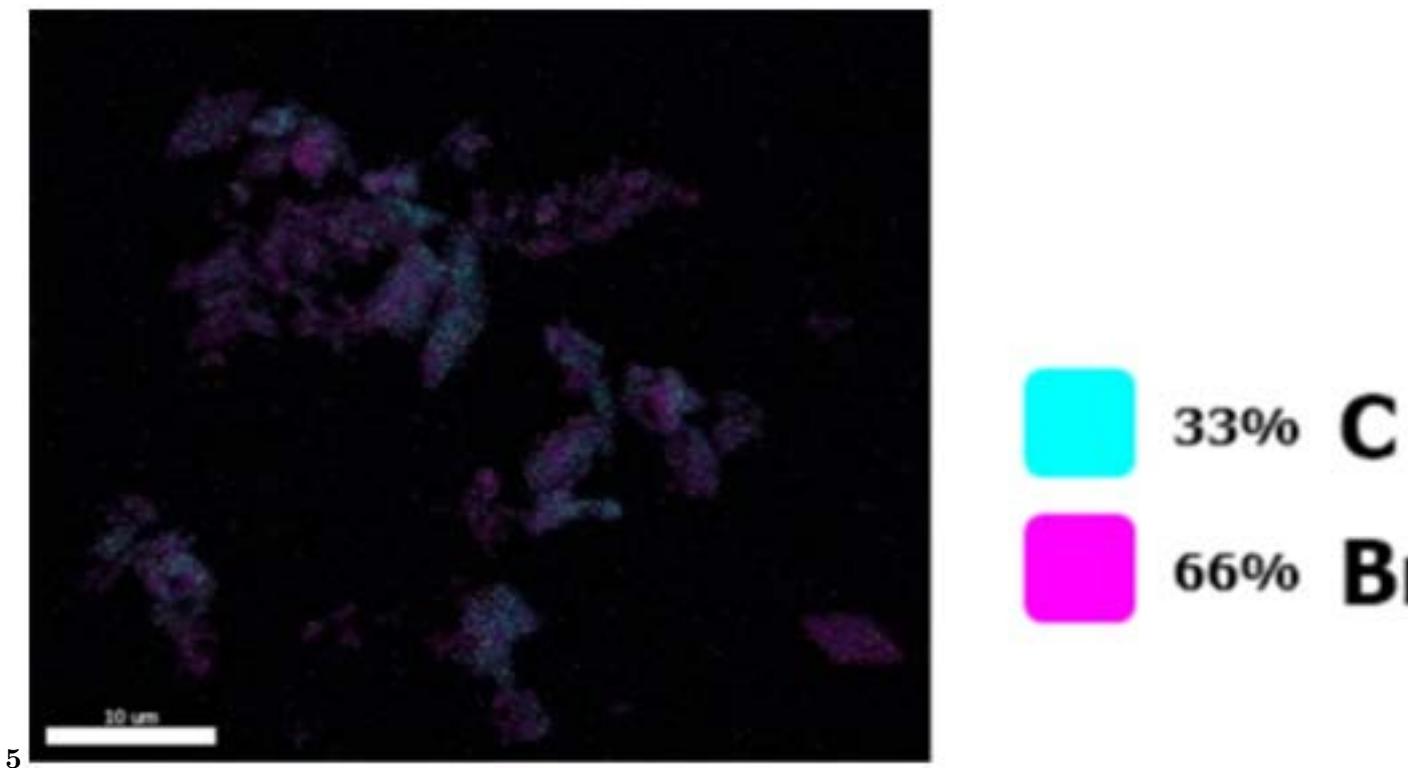
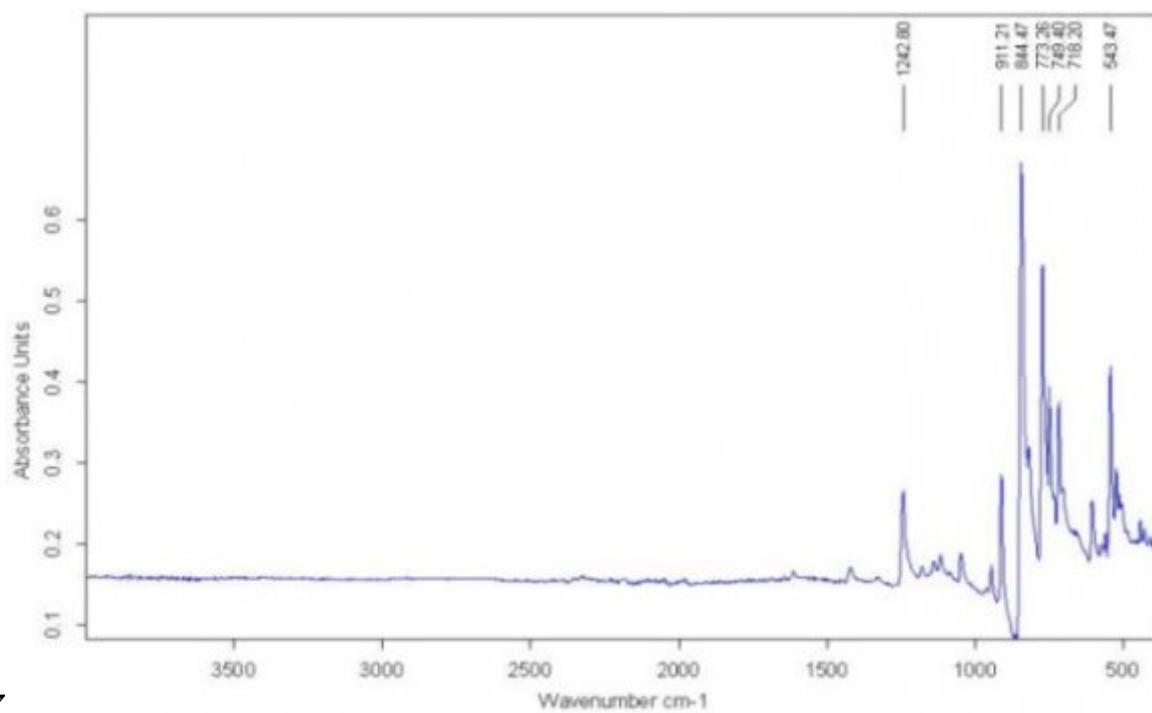
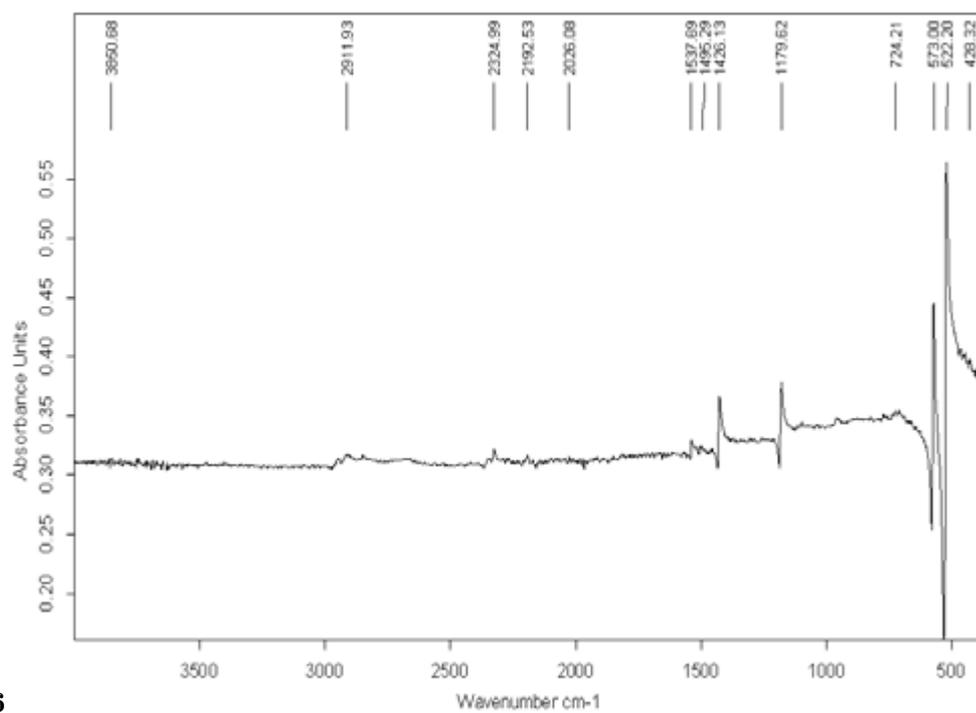


Figure 6: Fig. 5 :



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Figure 7: Fig. 7 :



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Figure 8: 1 Fig. 6 :

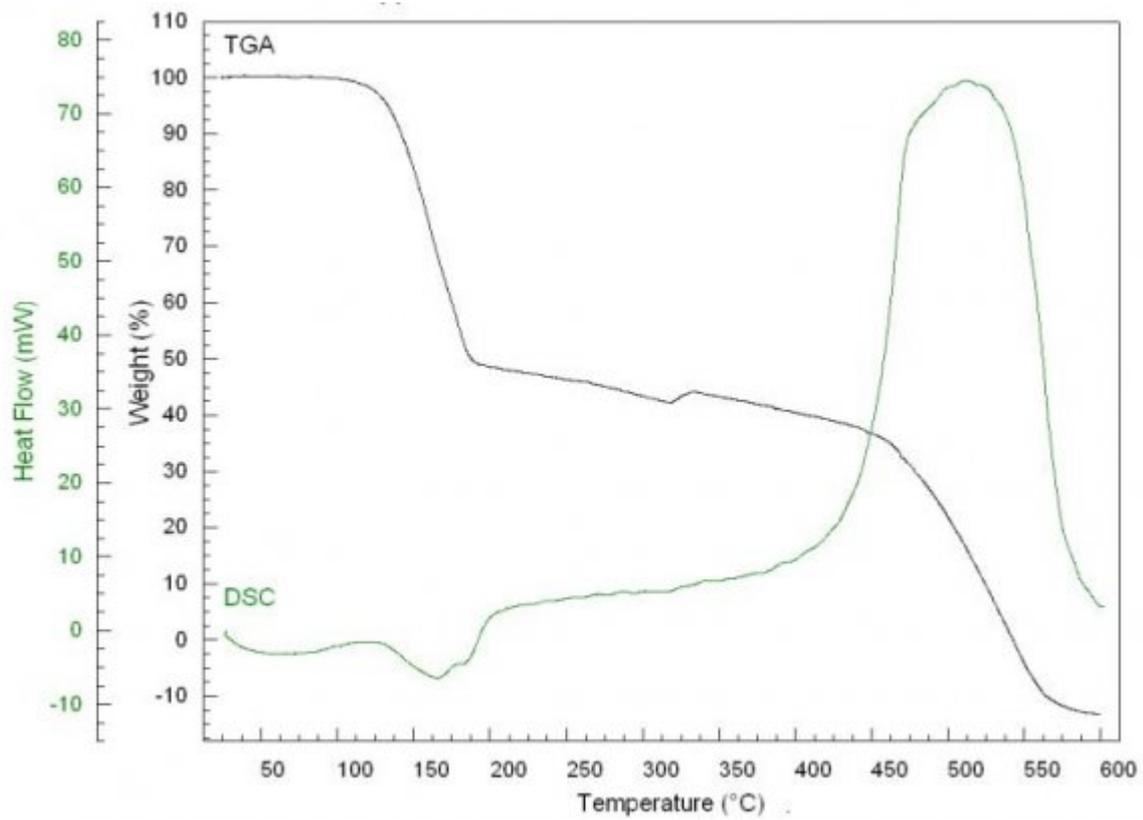
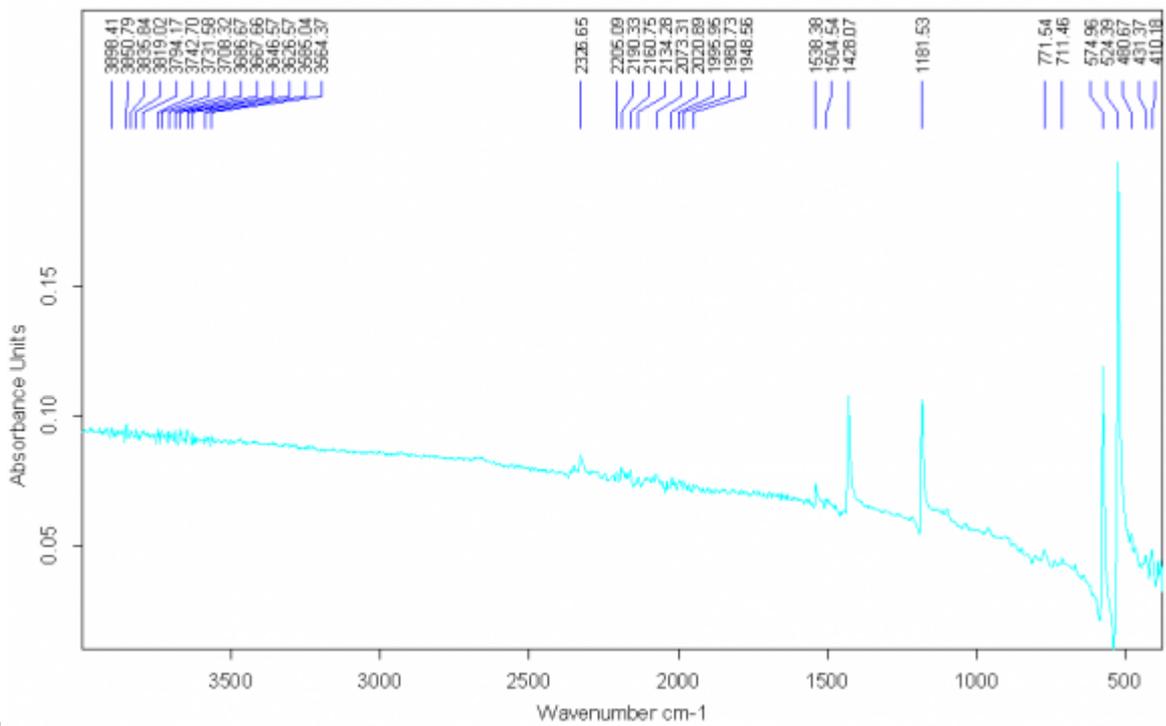
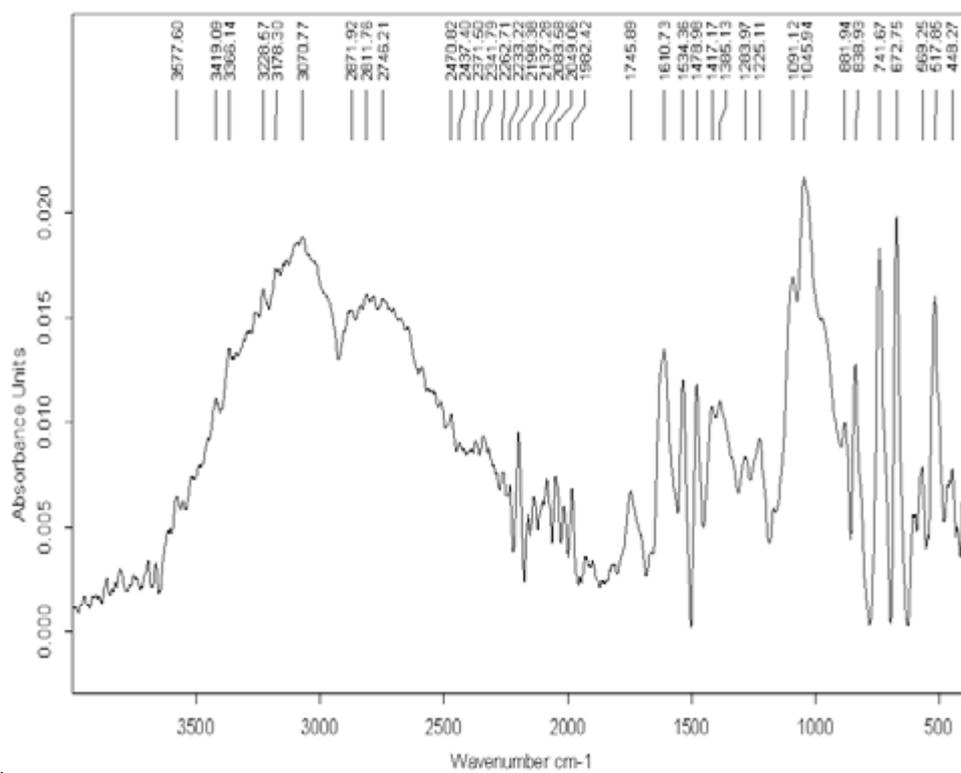


Figure 9:



11

Figure 10: Fig . 11 :



14

Figure 11: Fig. 14 :

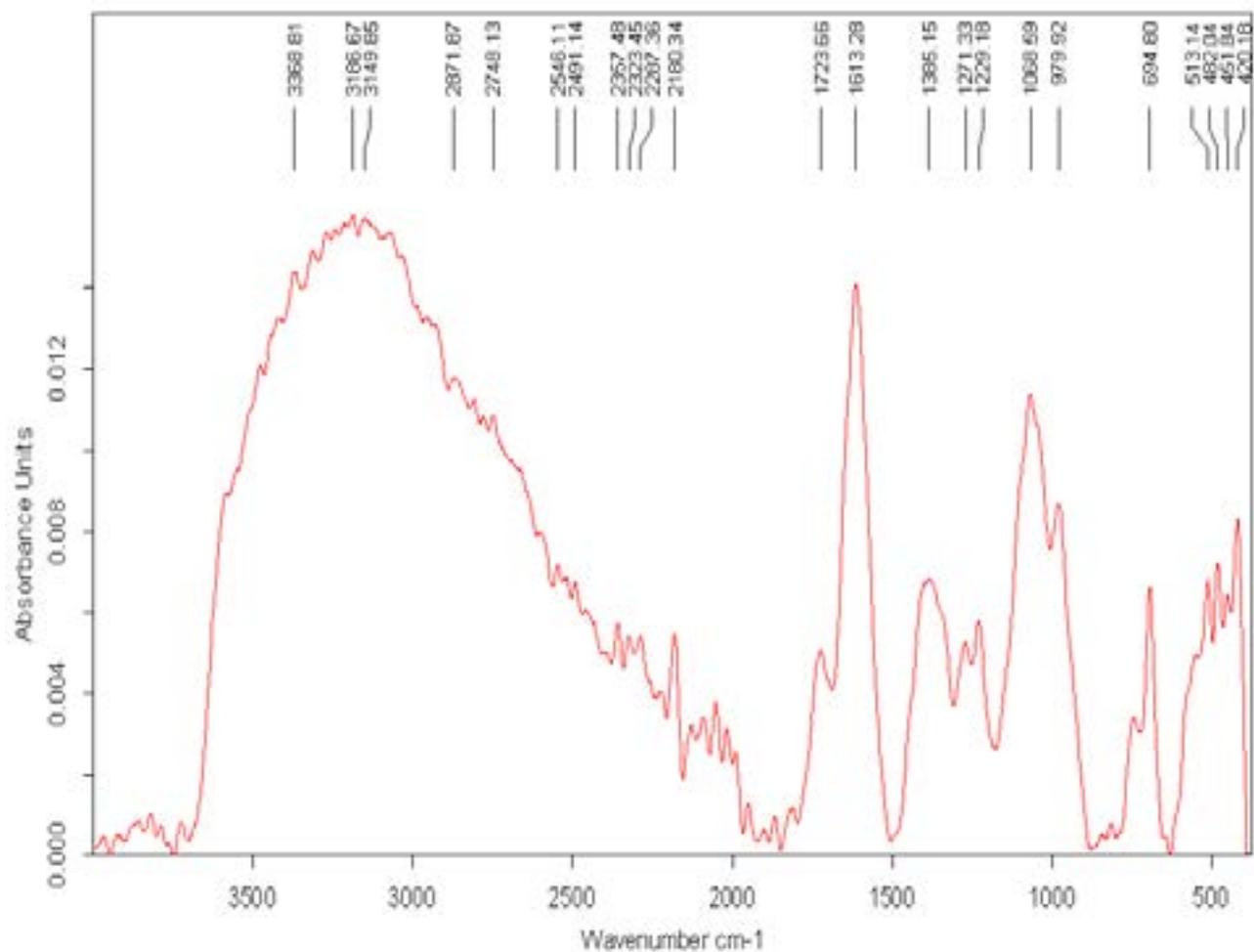


Figure 12:

1

SampleNo.	temperature intervals		Weight loss (%)
	Thermal processNo.	Temperature range (°C)	
GO-C 60 Brx (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 4	213.5 -222.3 222.3 -368.8	43.6 2.8
	5	368.8 -473.0	18.1
	6	473.0 -600.0	6.1

Figure 13: Table 1 :

2

Sample No.	Thermal process No.	Temperature range (°C)	$\hat{\Delta}H$ (kJ/kg) *	H (mW)	f1	ΔH (kJ/kg)
GO-C 60 Brx (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		

Figure 14: Table 2 :

4

Sample No.	Thermal effect No.	Temperature range (°C)	$\hat{\Delta}H$ (kJ/kg) *	H (mW)	f1	ΔH (kJ/kg)
GO-	1	25.0 -131.9	1288.6	32.0		
	2	131.9 -171.9	-180.1	21.8		-301.3
C 60 -Br	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		

$\hat{\Delta}H$ = thermal effect of the process based on DSC curves ($\hat{\Delta}H > 0$?endothermic process, $\hat{\Delta}H < 0$?exothermic process)

Figure 15: Table 4 :

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