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TECHNICAL SPECIFICATION

Nanomanufacturing – Key control characteristics –
Part 6-1: Graphene-based material – Volume resistivity: four probe method

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IEC Central Office
3, rue de Varembé
CH-1211 Geneva 20
Switzerland

Tel.: +41 22 919 02 11
info@iec.ch
www.iec.ch

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CONTENTS

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NANOMANUFACTURING –
KEY CONTROL CHARACTERISTICS –

Part 6-1: Graphene-based material –
Volume resistivity: four probe method

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Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-6-1, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

Draft TS	Report on voting
113/454/DTS	113/511/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts of the IEC TS 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

Graphene has attracted great interest as a next generation electronic material due to its extremely high mobility and ballistic transport of electrons [1][1]. The unique properties of graphene enable it to be an effective candidate used in electronic products such as transparent conducting films, sensors, field emitters, supercapacitors, etc.

Characterization of the electrical properties of graphene itself is essential to both manufacturers and users in order to develop innovative electronic devices or to improve existing electronic devices using it.

Commercialized graphene products can be categorized by their manufacturing methods as follows: (i) graphene flakes and/or nanoplatelets in powder form (hereinafter called GNP), (ii) graphene sheets suspended in liquids or (iii) graphene films grown by chemical vapour deposition (CVD).

Many electrical properties of a powder-type graphene product are significantly affected by its geometric and electronic parameters [2]. First, it is required to select the parameter that best represents the quality of the graphene products. Second, a suitable sample preparation for the purpose of electrical measurements is also elucidated and described. Finally, measurement conditions are also crucial factors to determine the representative value of the powder product in terms of its electrical properties.

Among the measurands in determining electronic properties of powder-type graphene – sheet resistance (or conductance), resistivity (or conductivity), volume resistivity (or volume conductivity), and so on – this document selects volume resistivity (or volume conductivity) for the representative measurand which reveals the electrical properties of powder-type graphene through a series of experiments.

This document describes a simple method to evaluate the volume resistivity (or volume conductivity) of powder-type graphene, which includes preparation of its pellet and a measurement method.

Case studies illustrating the application of the standard are provided in Annex A.

[1] Numbers in square brackets refer to the Bibliography.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-1: Graphene-based material – Volume resistivity: four probe method

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the electrical key control characteristic

– volume resistivity

  for powder consisting of graphene-based material like flakes of graphene, few layer graphene and/or reduced graphene oxide after preparation of a sample in pellet form by

– four probe method

  using powder resistivity measurement system.

The volume resistivity is a measure of the quality of powder-type graphene products in terms of electrical property and reflects the density-dependency shown in a pellet of powder-type graphene.

The volume conductivity can directly be derived from the volume resistivity.

Typical application areas are industries that use powder-type graphene products for graphene manufacture, potential developers, and users who produce graphene-based products. As the volume resistivity measured according to this document requires the preparation of a sample in the form of a pellet, this document describes in detail

– an apparatus to prepare consistently a test sample, the pellet,
– the preparation of the pellet starting from powder-type graphene,
– the measurement procedure to measure the volume resistivity (or volume conductivity) of the pellet, and
– the data analysis, the interpretation and reporting of the results.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

NOTE A comprehensive nanotechnology vocabulary is under ongoing development in IEC TC 113 and ISO/TC 229, in cooperation with ISO/TC 229. The vocabulary is being published as different parts of IEC TS 80004 and ISO/TS 80004. The terms and definitions in this document are harmonized with the terms and definitions of IEC 80004 (all parts) and ISO 80004 (all parts). They will remain harmonized during the maintenance of the document. Definitions not yet specified are taken from scientific literature.

3.1 General terms

3.1.1
graphene pellet
disc formed by compression of graphene powder

3.1.2
reduced graphene oxide
rGO
reduced oxygen content form of graphene oxide

Note 1 to entry This can be produced by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods or by exfoliating reduced graphite oxide.

Note 2 to entry: If graphene oxide was fully reduced then graphene would be the product. However, in practice, some oxygen containing functional groups will remain and not all sp^3 bonds will return back to sp^2 configuration. Different reducing agents will lead to different carbon to oxygen ratios and different chemical compositions in reduced graphene oxide.

[SOURCE: ISO/TS 80004-13:2017 [3], 3.1.2.14]

3.1.3
graphene-based material
GBM
graphene material
grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate, and functionalized variations thereof as well as graphene oxide and reduced graphene oxide

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

3.2 Key control characteristics

3.2.1
volume resistivity
<of pellet formed from graphene-based material> key control characteristic to describe the quality of powder-type graphene products

Note 1 to entry The measured volume resistivity of powder-type graphene products mainly depends on geometric factors such as flake size and layer numbers of a flake. As the applied pressure into a pellet increases, electrical contact among flakes is improved. The measurand "volume resistivity" reflects the density-dependency shown in a pellet of powder-type graphene-based material.

3.3 Terms related to measurements

3.3.1
volume conductivity
electrical conductivity
conductivity
σ
characteristic physical property of three-dimensional materials describing the ability to conduct electric current

Note 1 to entry The volume conductivity is defined by Ohm's law, $j = \sigma \times E$, where j is the current density measured in amperes per square metre (A/m^2) and E the electric field in volts per metre (V/m).

Note 2 to entry The volume conductivity can be obtained by dividing the surface conductance by the conductor thickness (t): $\sigma = \sigma_S/t$. The unit of measure of σ is siemens per metre (S/m).

[SOURCE: IEC TS 62607-6-4:2016, 3.2.3]

3.3.2
volume resistivity
electrical resistivity
resistivity
ρ
reciprocal of the volume conductivity

Note 1 to entry The volume resistivity is defined by Ohm's law, $j = \rho^{-1} \times E$, where j is the current density measured in amperes per square metre (A/m^2) and E the electric field in volts per metre (V/m).

Note 2 to entry The volume resistivity can be obtained by multiplying the surface resistance (ρ_s) by the conductor thickness (t): $\rho = \rho_s \times t$. The SI unit of ρ is the ohm metre ($\Omega\cdot$m).

3.3.3
surface conductance
sheet conductance
σ_s
characteristic physical property of two-dimensional materials describing the ability to conduct electric current

Note 1 to entry The SI unit of measure of σ_s is siemens (S). In the trade and industrial literature, however, siemens per square (S/square) is commonly used when referring to surface conductance. This is to avoid confusion between surface conductance and electric conductance (G), which share the same unit of measure:

$$G = I/U = \sigma_s\ (w/l).$$

Note 2 to entry The surface conductance (σ_s) can be obtained by normalizing conductance G to the specimen width (w) and length (l).

[SOURCE: IEC TS 62607-6-4:2016, 3.2.1]

3.3.4
surface resistance
sheet resistance
ρ_s
reciprocal of surface conductance

Note 1 to entry: ρ_s is a characteristic property of two-dimensional materials. The SI unit of measure of ρ_s is the ohm (Ω). In the trade and industrial literature, however, ohms per square (Ω/square) is commonly used when referring to surface resistance or sheet resistance.

[SOURCE: IEC TS 62607-6-4:2016, 3.2.4]

3.3.5
conductance
electrical conductance
G
reciprocal of the resistance

Note 1 to entry The conductance is defined by Ohm's law, $I = G \cdot U$, where I is the current through the conductor measured in amperes and U the potential difference along the conductor measured in volts.

Note 2 to entry The conductance is related to the material property conductivity σ by $G = A \times \sigma/L$, where A is the cross-section of the conductor in square metres and L its length in metres. The SI unit of G is siemens (S).

3.3.6
resistance
electrical resistance
R
ratio of the potential difference along a conductor and the current through the conductor

Note 1 to entry The resistance is defined by Ohm's law, $U = R \times I$, where I is the current through the conductor measured in amperes and U the potential difference along the conductor measured in volts.

Note 2 to entry The resistance is related to the material property resistivity ρ by $R = \rho \times L/A$, where A is the cross section of the conductor in square metres and L its length in metres. The SI unit of R is the ohm (Ω).

[SOURCE: ISO 15091:2012, 3.1]

3.3.7
four probe method
method to measure electrical sheet resistance, impedance or conductivity of thin films that uses separate pairs of current-carrying and voltage-sensing electrodes

Note 1 to entry The method is fast, repositionable and local.

[SOURCE: ISO/TS 80004-13:2017, 3.3.3.1, modified – The term "four-terminal sensing" has been deleted and the term "four point probe method" has been replaced by "four probe method".]

4 Sample preparation

For measurement of graphene powders using the four probe method, the sample should be prepared with uniform surface over a large area [4]. Two types of sample are suitable for this measurement: pellet or film. The sample shall be made in the form of a pellet because generating a uniform film from powder-type graphene is difficult due to its low solubility in any solvent.

Graphene powder obtained from commercial sources is pelletized after vacuum drying at 80 °C for 24 h in order to remove any remnant of water content in the sample.

5 Measurement of volume resistivity of graphene pellet

5.1 Description of the measurement apparatus

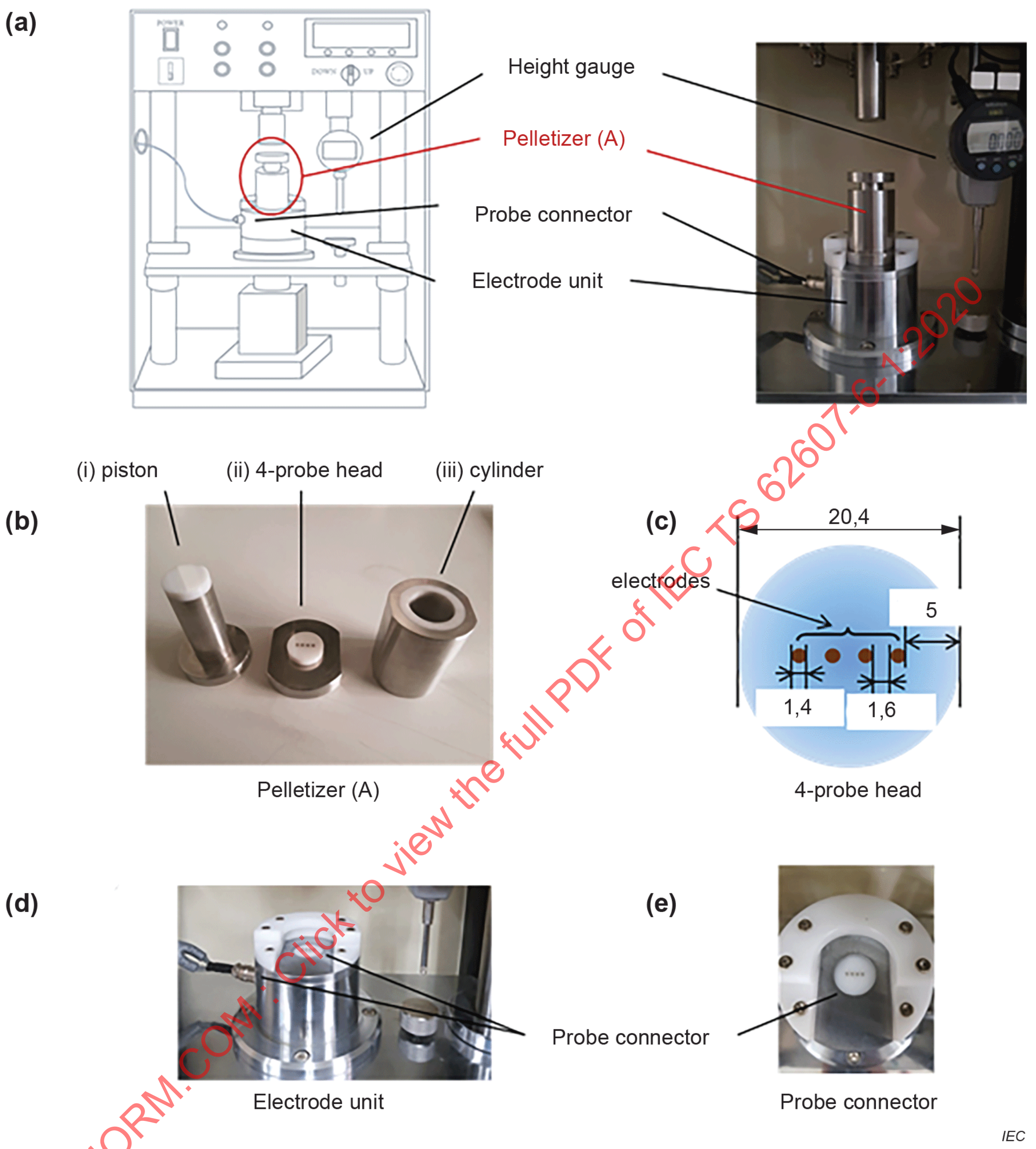
The powder resistivity measurement system consists of two components [5],[6]:

1) a pelletizer and electrode unit;
2) an electrical measurement system.

The details of the measurement system are shown in Figure 1.

A pelletizer is composed of a four-probe head, a piston, and a cylinder. The head of the piston and the inside of the cylinder are covered with a non-conducting material, zirconia, so that the specimen is electrically isolated from all sides. The pelletizer is electrically connected to a four-probe unit through a probe connector. The four-probe setup consists of four equally-spaced copper or gold rods with identical radius. The inner diameter of the cylinder is 20,4 mm, the probe spacing is 1,6 mm, and the diameter of each of the four electrodes is 1,4 mm. The applied pressure is measured by a pressure gauge with high precision for a maximum pressure of 52 MPa. A height gauge is used to measure the height of the piston at a given pressure. The height difference before and after pressurizing is referred to as the pellet thickness.

Dimensions in millimetres



(a) Schematic diagram and the photo of the powder resistivity measurement system

(b) Pelletizer equipped with a four-probe head and piston

(c) Top view of a four-probe head with dimensions

(d) Electrode unit

(e) Probe connector

Figure 1 – Measurement system

5.2 Determination of sample amount

It is important to maintain uniform thickness of a sample pellet, especially under high pressure. Otherwise electrical contact between the four-probe head at the bottom and the upper electrode will be made and result in electrical leakage. In order to avoid the experimental errors by the electrical leakage, the minimum thickness of the pellet, which is the thickness at the maximum pressure, should be determined. The thickness of the pellet can be calculated by consideration of graphene density, the inner diameter of the cylinder, and sample amount. In this calculation, it is assumed that density of the graphene pellet is the same as the theoretical density of graphite, 2,3 g/cm^3 [7]. Then the thickness (t) can be calculated by Equation (1):

$$t = m\,/(d_{gr} \times A) \tag{1}$$

where

t is the specimen (pellet) thickness measured by thickness gauge equipped in the apparatus;

d_{gr} is the theoretical density of graphite (2,3 g/cm^3);

m is the dose of sample;

A is the cross-sectional area of the piston.

The minimum thickness at the specific dose of sample is calculated by Equation (1) and summarized in Table 1.

Table 1 – Minimum thickness of the pellet vs amount of the used sample at the maximum applied pressure

Dose of sample (g)	t (mm)
0,1	0,146
0,2	0,293
0,3	0,439
1,0	1,465

5.3 The measurement procedures

After determining the amount of the powder-type graphene sample for the measurement, the powder sample is charged inside the cylinder (iii) which is assembled with probe head (ii). Then, after tapping the sample cylinder in order to uniformly distribute the powder for a flat surface, the piston (i) is placed on the flat surface. Finally, the sample-charged pelletizer is connected to the electrode unit, then a pressure from 2,6 MPa to 52 MPa with 2,5 MPa interval is applied to the pelletizer. While pressurizing, the resistance values are recorded via the four-probe system, at given pressures. The volume resistivity is calculated by the consideration of the pellet thickness, which is measured simultaneously with sheet resistance. For confirmation of reliability and reproducibility, it is recommended to conduct the test three times using different samples for each batch.

6 Data analysis and interpretation of results

6.1 General

The volume resistivity, the target parameter of this document, reflects the quality of a sample product in terms of electrical properties. The target measurand can be measured by a series of resistivity measurements as a function of density of pellet. Resistivity of the various products of powder-type graphene has been measured as a function of density.

6.2 Analysis of volume resistivity as a function of the applied pressures

The resistivity of a pellet is mainly controlled by geometric dimensions of components in a sample, especially its thickness in here which is correlated with the applied pressure. Hence, the volume resistivity may imply the geometric factors which are different from powder-type graphene products. The volume resistivity of a pellet is calculated by Equation (2):

$$\rho_{\mathrm{v}} = R \times F \times t \tag{2}$$

where

ρ_{v} is the volume resistivity;

R is the resistance measured by 4-probe measurement system ($R = V/I$);

t is the specimen(pellet) thickness measured by thickness gauge equipped in the apparatus;

F is the geometrical correction factor [8],[9].

6.3 Calculation of volume conductivity of a pellet

The volume conductivity of a pellet is calculated by Equation (3):

$$\sigma_{\mathrm{v}} = 1/\rho_{\mathrm{v}} \tag{3}$$

where

σ_{v} is the volume conductivity;

ρ_{v} is the volume resistivity calculated from Equation (2).

6.4 Analysis of volume resistivity (or volume conductivity) as a function of the volume density of graphene pellet

In case of powder-type graphene, thickness of its pellet is significantly affected by the dose of a sample. Accordingly, its density should be considered in evaluating the electrical property of powder-type graphene.

The volume density of a graphene pellet (d_{v}) at the given pressure is calculated from the mass of a pellet and its geometric dimension described in Equation (4) [5].

$$d_{\mathrm{v}} = m/V = m/(A \times t) \tag{4}$$

where

d_{v} is the volume density of a graphene pellet;

m is the mass of the specimen;

V is the volume of the pellet;

A is the cross-sectional area of the piston;

t is the specimen (pellet) thickness measured by thickness gauge equipped in the apparatus.

7 Report

The report includes the following:

- sample preparation;
- measurement procedure;
- table of thickness (t) and volume density (d_V) of graphene pellet, sheet resistance (ρ_S), volume resistivity (ρ_V), and volume conductivity (σ_V) under each applied pressure value;
- plot of pressure (P) vs ρ_V or σ_V;
- plot of volume density of graphene pellet (d_V) vs ρ_V or σ_V;
- ρ_V or σ_V under two or more different volume densities including the calculated value at the maximum applied pressure.

Annex A
(informative)

Case studies

A.1 Graphene (reduced graphene oxide (rGO) and graphene nanopowder (GNP))

Three types of powder-type graphene were used in these case studies, namely, i) two commercialized brands labelled as rGO by their manufacturers and ii) graphene nanopowder (GNP) which is also commercially available. The graphene products are confirmed by their thickness information in terms of the number of layers provided by manufacturers. According to the material specification, the rGO includes flakes in one or two layers while the GNP consists of flakes of 1,6 nm thickness (between two and four graphene layers). The graphene powders were dried under vacuum at 80 °C for 24 h before the powder resistivity measurements.

A.2 Morphology change of rGO flakes before and after pressurization

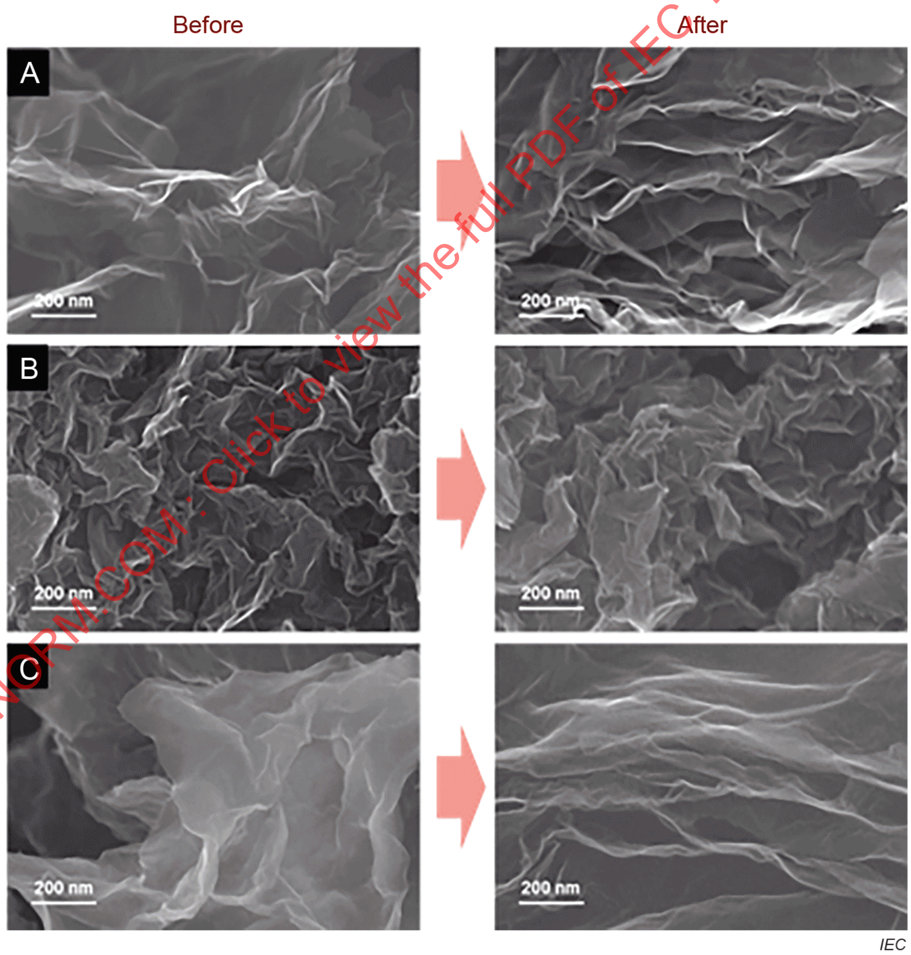


Figure A.1 – FE-SEM images of rGO flakes of (A) Company 1 (rGO-A), (B) Company 2 (rGO-B) and (C) graphene nanopowder (GNP) before (left) and after (right) pressurization

The morphology of the three samples was observed by field emission scanning electron microscope (FE-SEM) without any sample pre-treatment. The FE-SEM images of the three samples before and after pressurization up to 52 MPa are exhibited in Figure A.1. Commonly it is observed that corrugation among the flakes is enhanced by pressurization and can be correlated to the conductivities of the samples. A critical deformation via the pressurization is not observed in the microscopic study in any of the samples.

A.3 Raman spectroscopy measurement of graphene powder before and after pressurization up to 52 MPa

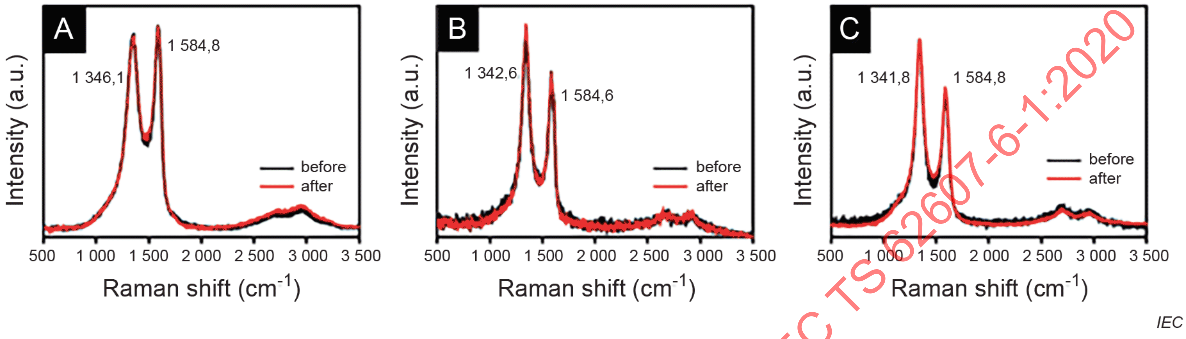


Figure A.2 – Raman spectra of (A) rGO-A, (B) rGO-B and (C) GNP before (black line) and after (red line) pressurization

The structural changes in the sample before and after the pressurization are investigated by Raman spectroscopy that was performed at an excitation wavelength of 532 nm. Figure A.2 displays the representative Raman spectra of the three graphene samples before and after pressurization. Each sample was measured at five different locations and the intensity of each peak was normalized to the G-band intensity. The Raman spectra of the graphene samples exhibit tangential breathing modes (G-band) at 1 584 cm^{-1} and disorder modes (D-band) at approximately 1 340 cm^{-1}. The intensity ratio between D-band and G-band (I_D/I_G) is generally considered to evaluate the surface damage or structural deformation of graphene [10]. The possible structural deformations before and after pressurization were examined through the changes in the I_D/I_G. A significant variation in the ratio was not observed in the three types of graphene, which implies no significant alteration in their structures (Figure A.3).

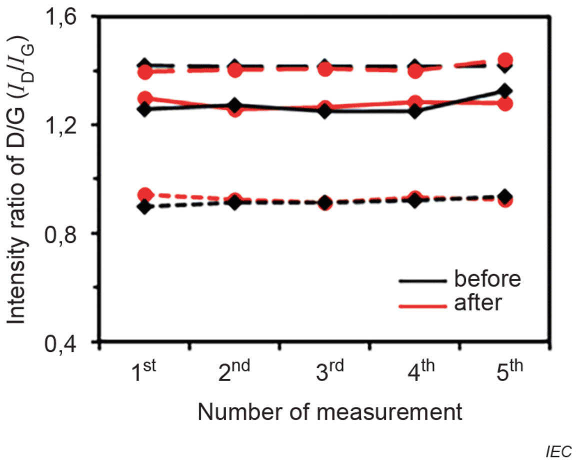


Figure A.3 – Comparison data for I_D/I_G of rGO-A (short-dash line), rGO-B (solid line) and GNP (long-dash line) before and after pressurization

A.4 Results on powder resistivity measurements

A.4.1 Powder resistivity measurement of rGO-A (company 1) with various amounts

Table A.1 – An example of the measurement parameters for rGO-A (0,2 g)

Pressure (MPa)	t (mm)	d (g/cm^3)	ρ_s (Ω/sq)	ρ_v (Ωm)	σ_v (S/m)
2,61	2,643	0,232	4,37	$1,15 \times 10^{-2}$	87
5,16	1,758	0,348	2,83	$4,98 \times 10^{-3}$	201
7,74	1,279	0,479	2,40	$3,07 \times 10^{-3}$	326
10,32	1,038	0,590	2,10	$2,18 \times 10^{-3}$	458
12,90	0,874	0,700	1,97	$1,72 \times 10^{-3}$	581
15,48	0,770	0,795	1,86	$1,43 \times 10^{-3}$	699
18,06	0,687	0,891	1,80	$1,24 \times 10^{-3}$	809
20,63	0,619	0,989	1,73	$1,07 \times 10^{-3}$	932
23,21	0,566	1,081	1,70	$9,60 \times 10^{-4}$	1 042
25,79	0,531	1,152	1,65	$8,75 \times 10^{-4}$	1 142
28,37	0,491	1,246	1,62	$7,95 \times 10^{-4}$	1 257
30,97	0,464	1,319	1,58	$7,34 \times 10^{-4}$	1 362
33,54	0,432	1,416	1,56	$6,75 \times 10^{-4}$	1 481
36,12	0,409	1,496	1,54	$6,28 \times 10^{-4}$	1 593
38,70	0,387	1,581	1,52	$5,87 \times 10^{-4}$	1 705
41,28	0,364	1,681	1,51	$5,48 \times 10^{-4}$	1 824
43,85	0,344	1,779	1,50	$5,15 \times 10^{-4}$	1 942
46,44	0,327	1,871	1,49	$4,86 \times 10^{-4}$	2 056
49,02	0,312	1,961	1,48	$4,61 \times 10^{-4}$	2 169
51,57	0,297	2,060	1,46	$4,33 \times 10^{-4}$	2 308

Table A.1 shows an example of the series of the measurement parameters, such as applied pressure (P), pellet thickness (t), volume density of the pellet (d_v), sheet resistance (ρ_s) volume resistivity (ρ_v) and volume conductivity (σ_v) of the sample, with 0,2 g of rGO-A obtained by the measurement system. The resistance and pellet thickness values at the given applied pressure were measured by a digital multimeter and a thickness gauge, respectively. The surface resistance (ρ_s) was calculated by multiplying the resistance (R) by the geometrical correction factor (F) ($\rho_s = R \times F$). Here, the geometrical correction factor 4,294 is applied [8],[9]. The volume resistivity and conductivity of the pellet are calculated by Equations (2) and (3).

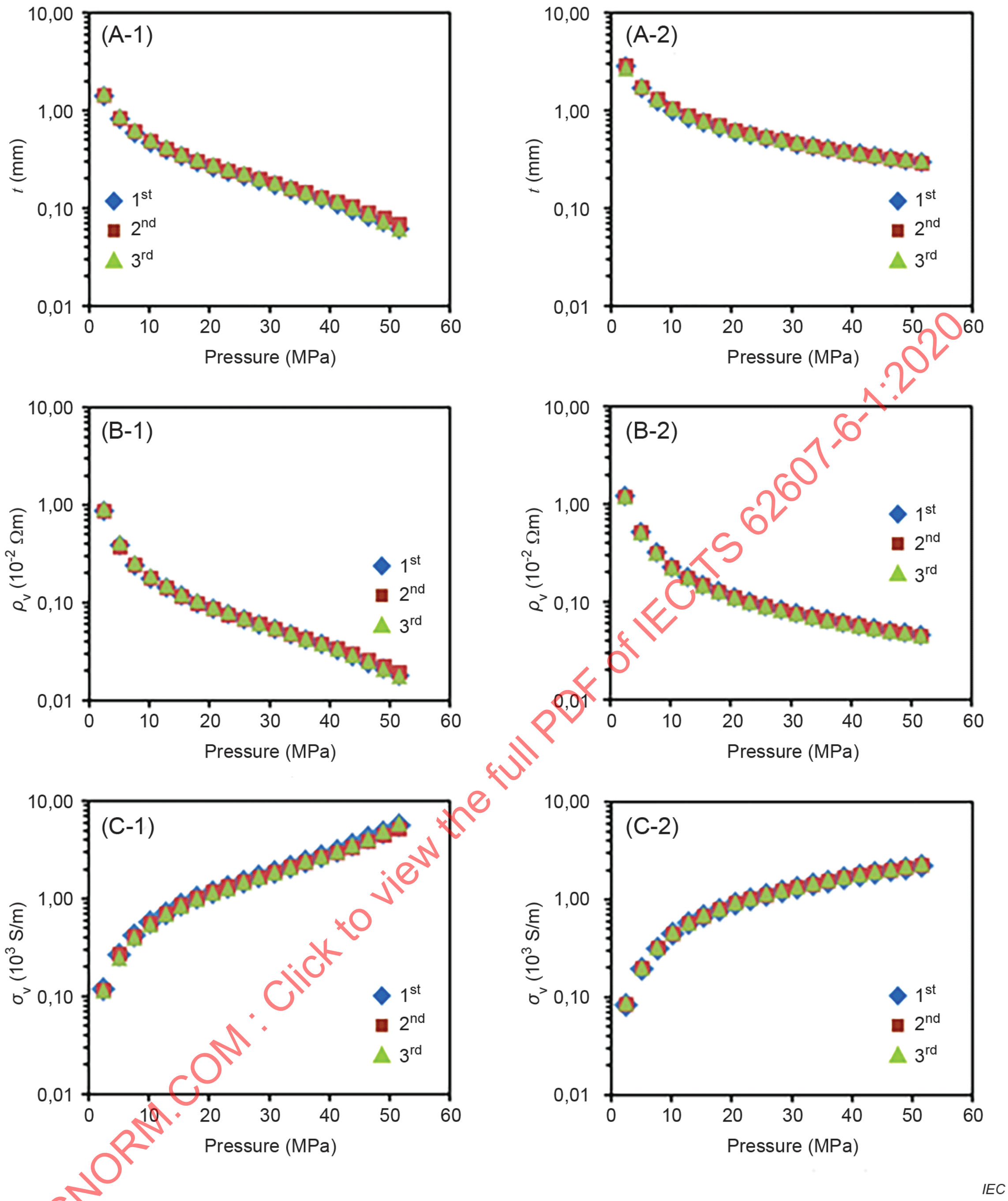


Figure A.4 – Correlation plots of (A) thickness, (B) volume resistivity (ρ_V), and (C) volume conductivity (σ_V) as a function of the applied pressure: (1) 0,1 g and (2) 0,2 g of rGO-A

In determining the intrinsic electrical behaviour of materials, the thickness of a sample is an essential parameter. The thickness and electrical conductivity changes of a graphene pellet (rGO-A) at the applied pressure up to 52 MPa are depicted in Figure A.4.

Since the thickness of a sample pellet at the applied pressure is changed by the dose of a sample, the thickness measurements are performed on the two different pellets made of 0,1 g and 0,2 g at the initial test. Each test was performed three times with three different samples from different batches. The correlation plots between the thickness, volume resistivity or volume conductivity and the applied pressure shown in Figure A.4 show good reproducibility for both pellets. As the amount of a sample increases, the thickness of graphene pellet at the given applied pressure increases (Figure A.4 (A)), volume resistivity increases (Figure A.4 (B)), while the conductivity decreases due to the increasing sample thickness (Figure A.4 (C)).

Compared to similar characteristic trend in correlation between the thickness and the applied pressure for both doses of the sample as shown in Figure A.4 (A), the correlation between the volume conductivity and the applied pressure shows different trend from each other above 40 MPa (Figure A.4 (C)). Hence, it is better to determine electrical properties other than electrical conductivity, that are not dependent on sample thickness.

Figure A.5 shows the plot of the volume resistivities and volume conductivities of the two pellets as a function of their volume density (d_V). The reproducibility is confirmed by performing the measurements three times for each case.

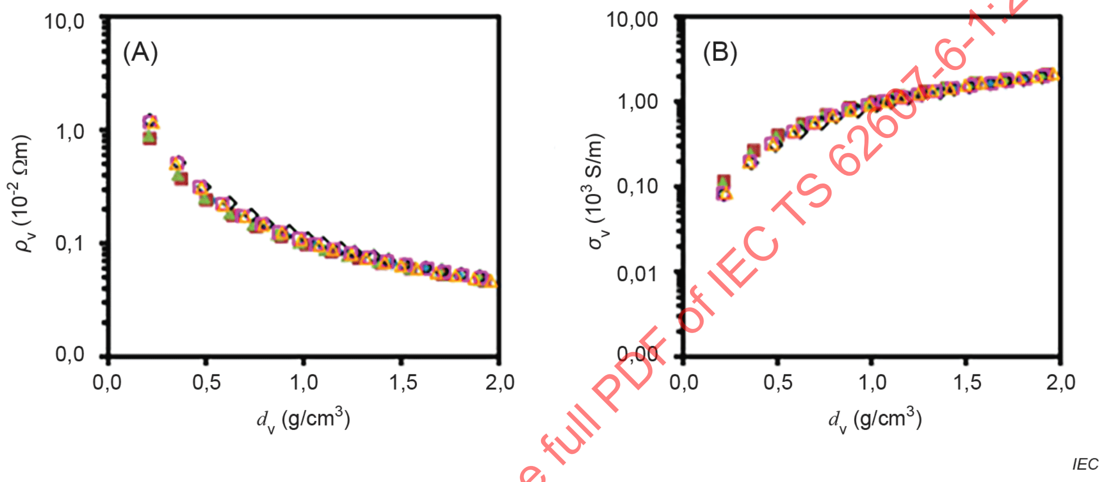


Figure A.5 – Correlation plots of (A) volume resistivity (ρ_V) and (B) volume conductivity (σ_V) as a function of the volume density (d_V) of a graphene pellet: 0,1 g (filled symbol) and 0,2 g (unfilled symbol) of rGO-A

The volume density of a graphene pellet at the applied pressure is calculated by Equation (4). According to the results, both the volume resistivity and volume conductivity as a function of the volume density are intrinsic since they are not dependent on the amount of sample.

A.4.2 Powder resistivity measurement of 1,0 g of rGO-B (company 2)

The results of the case studies on rGO-B (company 2) with the same analysis are shown in Figure A.6 and Figure A.7.

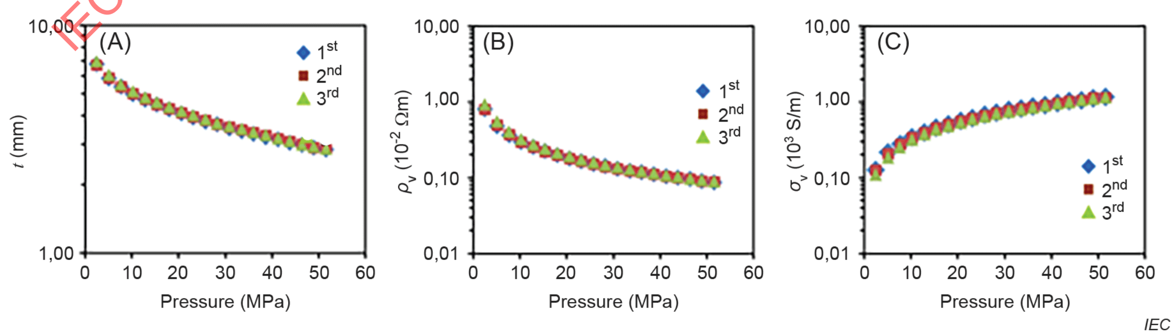


Figure A.6 – Correlation plots of (A) thickness (t), (B) volume resistivity (ρ_V), and (C) volume conductivity (σ_V) of rGO-B (1,0 g) as a function of the applied pressure

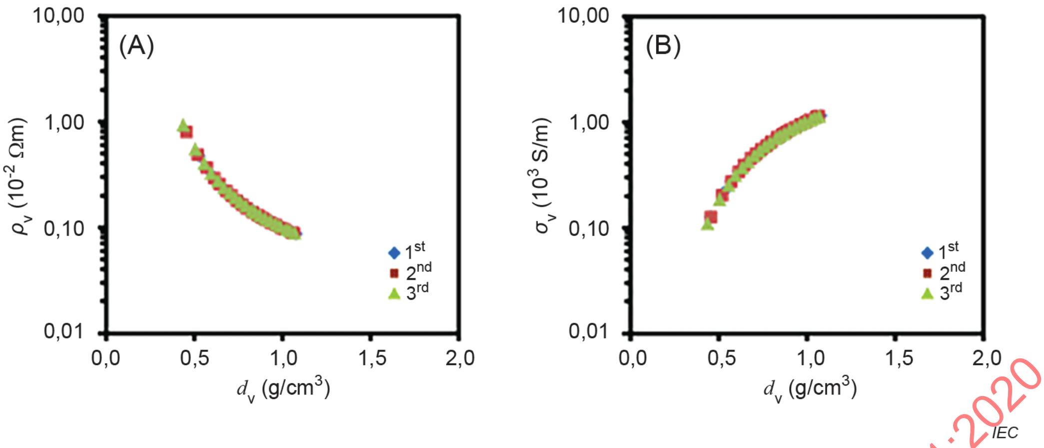
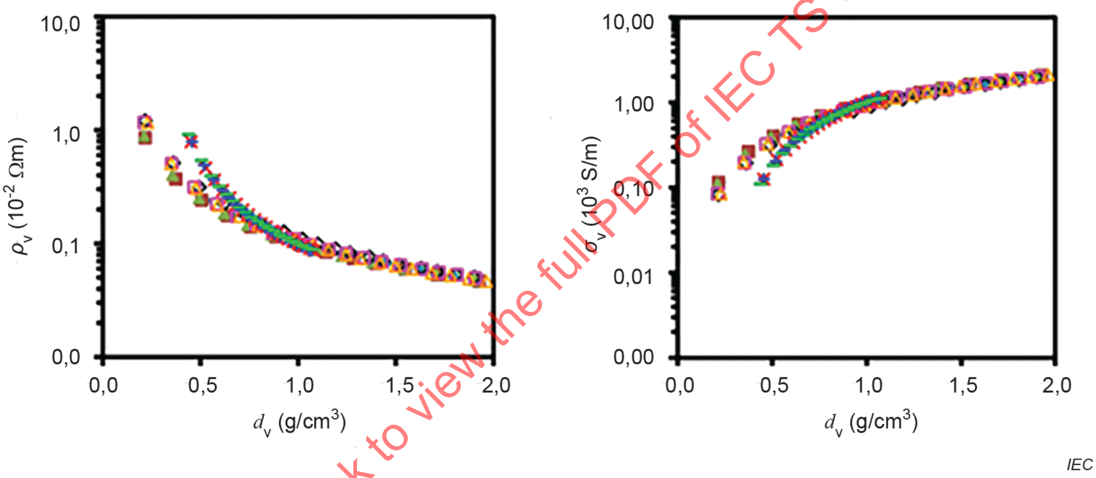


Figure A.7 – Correlation plots of (A) volume resistivity (ρ_V) and (B) volume conductivity (σ_V) of rGO-B (1,0 g) as a function of the volume density (d_V) of the graphene pellet



(A) **(B)**

Figure A.8 – Correlation plots of (A) volume resistivity (ρ_V) and (B) volume conductivity (σ_V) as a function of the volume density (d_V)of graphene pellets: 0,1 g (filled symbol), 0,2 g (unfilled symbol) of rGO-A and 1,0 g (lined symbol) of rGO-B

Figure A.8 shows the plot of the volume resistivities and volume conductivities of the pellets formed from rGO-A and rGO-B as a function of their volume density. The reproducibility is confirmed by performing the measurements three times for each case. According to the results, both the volume resistivity and conductivity of rGO-B around pellet density 1 g/cm^3, which is the value at maximum applied pressure (50 MPa), become similar to those of rGO-A. The representative values of volume resistivity and volume conductivity of the two rGOs would be determined and compared under at least two different pellet densities including maximum calculated pellet density. The representative volume resistivity and conductivity under different pellet densities of the two rGOs are tabulated in Table A.2.

Table A.2 – Volume resistivity and volume conductivity of rGO pellets

Sample		d_v = 1,00 g/cm^3	d_v = 1,08 g/cm^3	d_v = 2,00 g/cm^3
rGO-A	ρ_v (Ωm)	$1,00 \times 10^{-3}$ ($\pm$ $2,05 \times 10^{-5}$)	$9,17 \times 10^{-4}$ ($\pm$ $1,87 \times 10^{-5}$)	$4,60 \times 10^{-4}$ ($\pm$ $9,47 \times 10^{-6}$)
	σ_v (S/m)	$9,97 \times 10^{2}$ ($\pm$ $2,01 \times 10^{1}$)	$1,09 \times 10^{3}$ ($\pm$ $2,21 \times 10^{1}$)	$2,18 \times 10^{3}$ ($\pm$ $4,43 \times 10^{1}$)
rGO-B	ρ_v (Ωm)	$1,00 \times 10^{-3}$ ($\pm$ $1,12 \times 10^{-5}$)	$9,52 \times 10^{-4}$ ($\pm$ $1,09 \times 10^{-5}$)	-
	σ_v (S/m)	$1,00 \times 10^{3}$ ($\pm$ $1,12 \times 10^{1}$)	$1,13 \times 10^{3}$ ($\pm$ $1,31 \times 10^{1}$)	-

A.4.3 Powder resistivity measurement of GNP

The results of the case studies on GNP with the same analysis with those of rGOs are exhibited in Figure A.9 and Figure A.10.

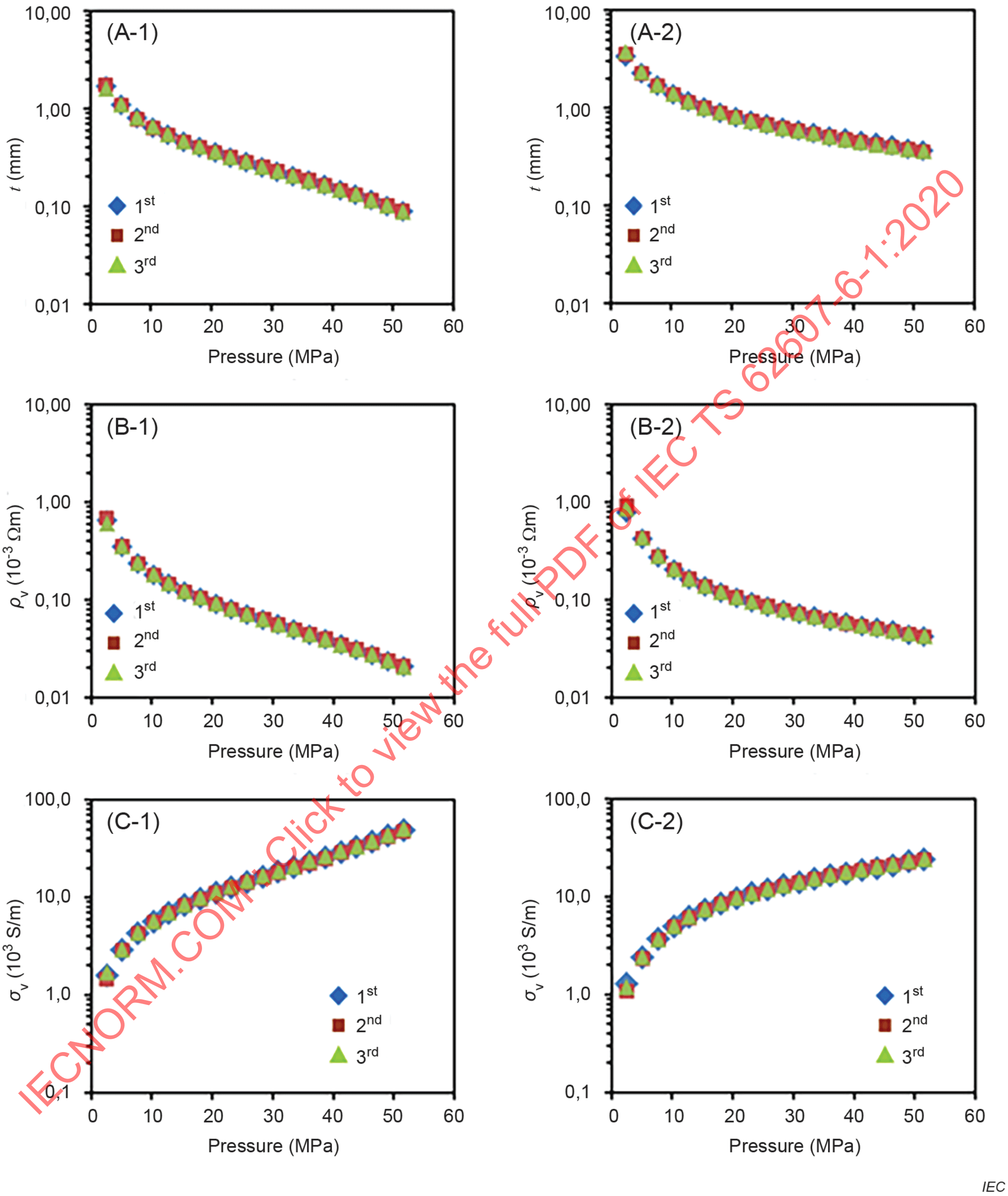


Figure A.9 – Correlation plots of (A) thickness (t), (B) volume resistivity (ρ_V), and (C) volume conductivity (σ_V) as a function of the applied pressure: (1) 0,1 g and (2) 0,2 g of GNP

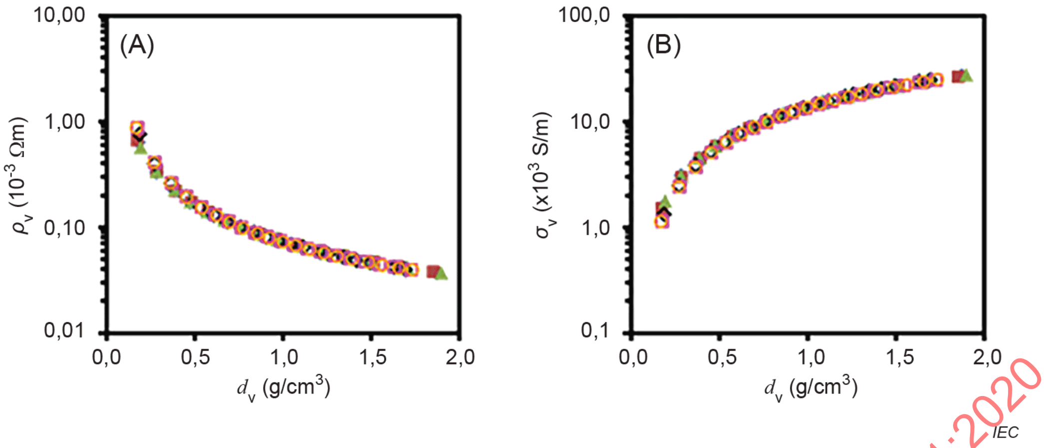


Figure A.10 – Correlation plots of (A) volume resistivity (ρ_V) and (B) volume conductivity (σ_V) as a function of the volume density (d_V) of a graphene pellet: 0,1 g (filled symbol) and 0,2 g (unfilled symbol) of GNP

Figure A.10 shows the plot of the volume resistivities and volume conductivities of the two GNP pellets as a function of their volume density. The reproducibility is confirmed by performing the measurements three times for each case. The representative volume resistivity and volume conductivity under the three different pellet densities are tabulated in Table A.3.

Table A.3 – Volume resistivity and volume conductivity of GNP pellets

Sample		d_v = 1,00 g/cm³	d_v = 1,50 g/cm³	d_v = 2,00 g/cm³
GNP	ρ_v (Ωm)	$7,31 \times 10^{-5}$ (± $5,66 \times 10^{-7}$)	$4,72 \times 10^{-5}$ (± $3,95 \times 10^{-7}$)	$3,49 \times 10^{-5}$ (± $3,02 \times 10^{-7}$)
	σ_v (S/m)	$1,37 \times 10^{4}$ (± $1,06 \times 10^{2}$)	$2,12 \times 10^{4}$ (± $1,78 \times 10^{2}$)	$2,87 \times 10^{4}$ (± $2,50 \times 10^{2}$)

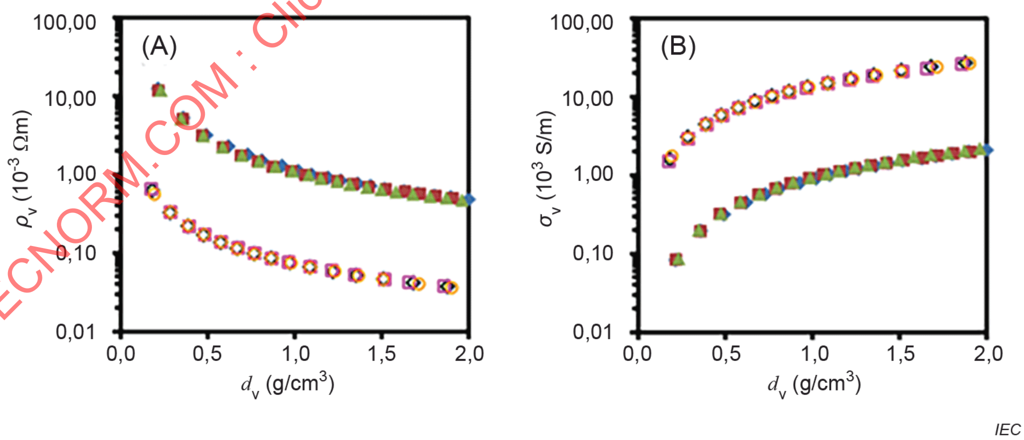


Figure A.11 – Comparison plots of (A) volume resistivity (ρ_V) and (B) volume conductivity (σ_V) as a function of the volume density (d_V) of graphene pellets: rGO-A (filled symbol) and GNP (unfilled symbol)

Figure A.11 shows the comparison plots of the volume resistivity and volume conductivity between rGO-A and GNP pellets as a function of their volume density. The volume conductivity under any density of graphene pellets of GNP is about 10 times larger than that of rGO-A due to larger oxygen content in rGO-A compared to GNP [11]. Figure A.12 and Table A.4 show x-ray photoelectron spectroscopy (XPS) survey spectra and calculated elemental analyses from the XPS peaks' areas.

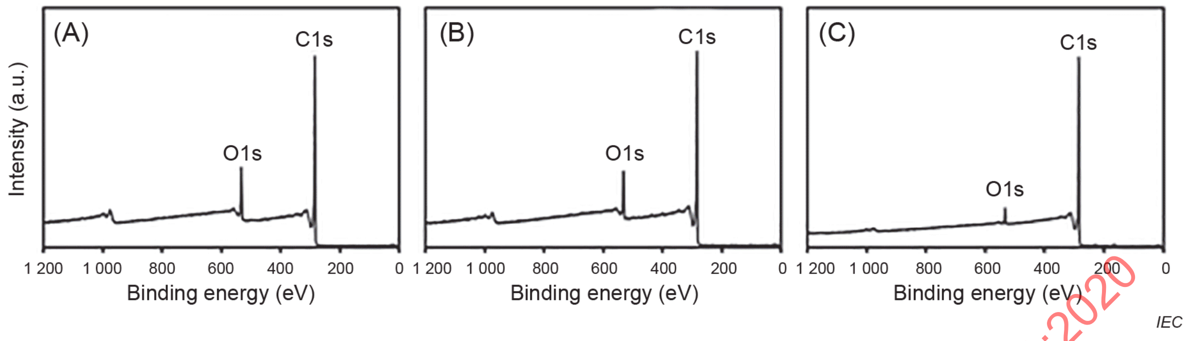


Figure A.12 – XPS survey spectra of as-received (A) rGO-A, (B) rGO-B and (C) GNP

Table A.4 – Summary of XPS data of three graphene samples in a powder form

Name	Binding energy (eV)	Atomic percentage (%)		
		rGO-A	rGO-B	GNP
C1s	284,60	86,11	86,09	94,28
Cl2p	201,88	0,03	0,11	
N1s	299,57	0,16	0,52	0,26
Na1s	1 071,50	0,17	0,14	0,04
O1s	533,28	13,02	12,21	4,27
S2p	168,41	0,21	0,30	0,81
Si2p	102,96	0,30	0,63	0,34

The volume resistivity and volume conductivity of the three graphene samples are summarized and compared in Table A.5.

Table A.5 – Volume resistivity (ρ_v) and volume conductivity (σ_v) of graphene pellets

Sample		d_v = 1,00 g/cm³	d_v = 1,08 g/cm³	d_v = 1,50 g/cm³	d_v = 2,00 g/cm³
rGO-A	ρ_v (Ωm)	$1,00 \times 10^{-3}$ ($\pm$ $2,05 \times 10^{-5}$)	$9,17 \times 10^{-4}$ ($\pm$ $1,87 \times 10^{-5}$)	$6,31 \times 10^{-4}$ ($\pm$ $1,30 \times 10^{-5}$)	$4,60 \times 10^{-4}$ ($\pm$ $9,47 \times 10^{-6}$)
	σ_v (S/m)	$9,97 \times 10^{2}$ ($\pm$ $2,01 \times 10^{1}$)	$1,09 \times 10^{3}$ ($\pm$ $2,21 \times 10^{1}$)	$1,59 \times 10^{3}$ ($\pm$ $3,22 \times 10^{1}$)	$2,18 \times 10^{3}$ ($\pm$ $4,43 \times 10^{1}$)
rGO-B	ρ_v (Ωm)	$1,00 \times 10^{-3}$ ($\pm$ $1,12 \times 10^{-5}$)	$9,52 \times 10^{-4}$ ($\pm$ $1,09 \times 10^{-5}$)	-	-
	σ_v (S/m)	$1,00 \times 10^{3}$ ($\pm$ $1,12 \times 10^{1}$)	$1,13 \times 10^{3}$ ($\pm$ $1,31 \times 10^{1}$)	-	-
GNP	ρ_v (Ωm)	$7,31 \times 10^{-5}$ ($\pm$ $5,66 \times 10^{-7}$)	$6,72 \times 10^{-5}$ ($\pm$ $5,30 \times 10^{-7}$)	$4,72 \times 10^{-5}$ ($\pm$ $3,95 \times 10^{-7}$)	$3,49 \times 10^{-5}$ ($\pm$ $3,02 \times 10^{-7}$)
	σ_v (S/m)	$1,37 \times 10^{4}$ ($\pm$ $1,06 \times 10^{2}$)	$1,49 \times 10^{4}$ ($\pm$ $1,18 \times 10^{2}$)	$2,12 \times 10^{4}$ ($\pm$ $1,78 \times 10^{2}$)	$2,87 \times 10^{4}$ ($\pm$ $2,50 \times 10^{2}$)

A.4.4 Powder resistivity measurement of graphene oxides with different amounts of oxygen

The results of the case studies on four types of graphene oxide (G-a, G-b, G-c, and G-d) with different oxygen amounts are shown in Figure A.13 to Figure A.17 Its reproducibility is confirmed by performing the measurements three times for each case.

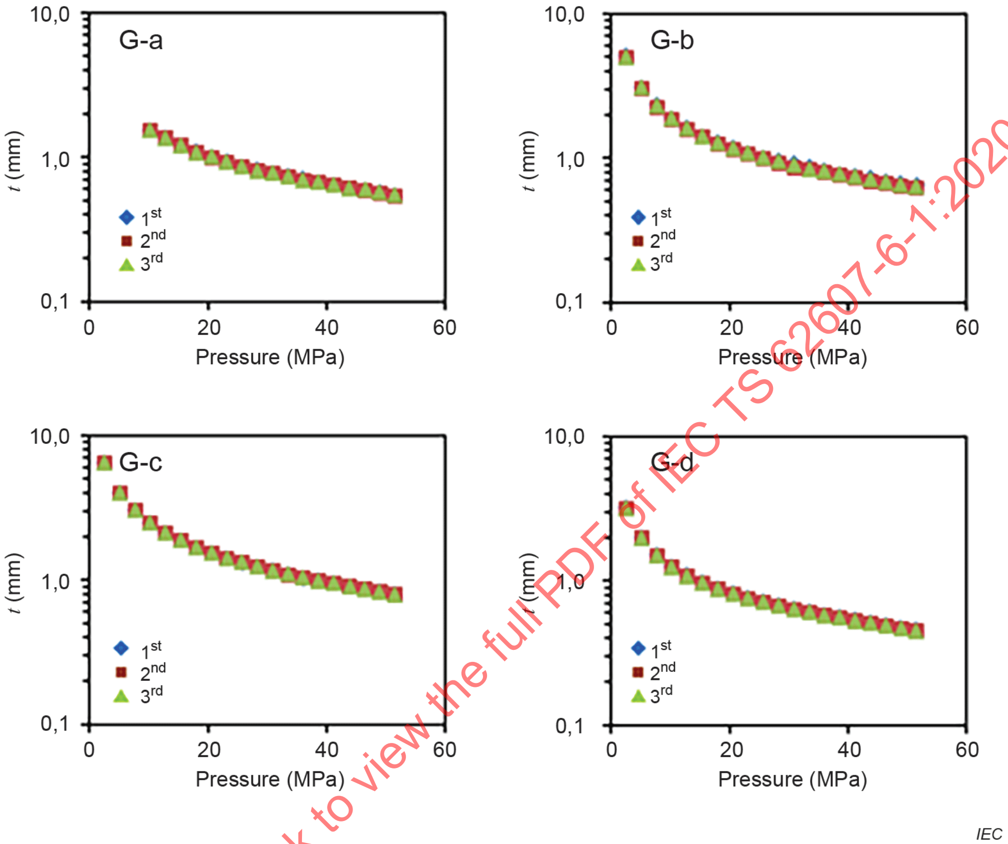


Figure A.13 – Correlation plots of thickness (t) as a function of the applied pressure: 0,3 g samples of four types of graphene oxide (G-a, G-b, G-c, and G-d)