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STRATEGIES FOR IMPROVING THE SHIELDING EFFECTIVENESS AND ELECTRICAL RESISTIVITY OF INJECTED THERMOPLASTIC COMPOSITES

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DISSERTAÇÃO DE MESTRADO APRESENTADA
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Master in Chemical Engineering

Strategies for improving the shielding effectiveness and electrical resistivity of injected thermoplastic composites

Master dissertation

of

Vítor Hugo Dias Telheiro

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Bosch Car Multimedia Portugal, S.A

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Abstract

Automotive manufacturers aim to reduce vehicles weight due to stricter legislation for lower fuel consumption and CO_2 emissions. Accordingly, there is an interest in searching for lightweight materials to replace high-density materials like metals. Electronic enclosures are one part of the car where the replacement of metals is being investigated, and for that, it is mandatory to fulfil some requirements for automotive applications. For electronic applications, it is necessary to ensure electromagnetic compatibility on the final product, i.e. should not be disrupted by or cause disruption in other electronic devices placed in the involving electromagnetic environment. Electrical conductivity is also an important material property to promote good grounding in the enclosure and electrostatic discharge (ESD) protection. The leading solution of lower density materials is by using thermoplastic composites. The selected commercial thermoplastic composites were subject to different tests to investigate their capability to replace metals.

Electromagnetic interference shielding effectiveness was studied in the range of 10 MHz to 6 GHz, for seven commercial injected thermoplastic composites. The best performance was for materials with nickel-coated carbon-fibres. Volumetric electrical resistivity was also evaluated with good results from the materials with PBT matrixes. Superficial electrical resistivity was measured accordingly to the four-point technique in two directions: perpendicular and parallel to the injection direction not being noticeable any filler preferred alignment on the surface. Three of the seven materials where selected based on their combination of properties to improve the surface resistivity and electrical contact by selected post-processing operations. Electrical resistivity was measured for these three materials through the impedance method. Laser ablation was then performed on three materials (A, B and C), the ones which have better shielding effectiveness, and the results were identical to those of non-ablated previously measured samples. When using impedance to determine resistance and afterwards resistivity the results are different. For material A and C the volumetric electrical resistivity decreased after laser ablation. Lastly, a metallic coating of copper was applied to the laser ablated samples and the electrical resistivity increased. For Material A the impedance method was used again and in this one the electrical resistivity was reduced.

With this project, it was possible to find commercially available thermoplastic composites with carbon-fibres that could perform accordingly to the requirements for automotive industry. They present a promising solution that can replace metals in electronic enclosures while having lower densities.

Keywords: Electromagnetic compatibility; Electromagnetic interference; Thermoplastics; Shielding; Resistivity

Resumo

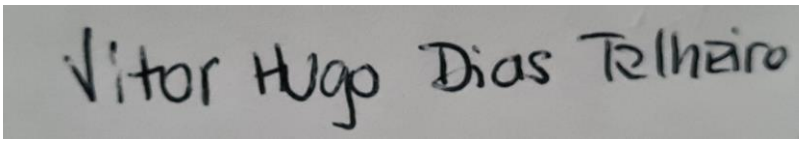
A indústria automóvel tem vindo a tentar reduzir o peso dos veículos devido a novas legislações que são cada vez mais restritas. Estas apontam para a redução do consumo de combustível e da emissão de gases de efeito de estufa. Posto isto, há um incentivo na procura de materiais mais leves para substituir materiais de alta densidade, nomeadamente os metais, em diversos compontentes dos automóveis. As *housings* eletrónicas tem sido um dos focos para realizar essa substituição, e para esse efeito, os novos materiais devem cumprir os requisitos da indústria automóvel. Compatibilidade eletromagnética no produto final é um dos principais requesitos, para que o seu funcionamento não seja perturbado ou perturbe o funcionamento de outros dispositivos. A condutividade elétrica é também uma propriedade importante que o material deve apresentar de modo a garantir bom *grounding* em toda a *housing* e evitar descargas eletrostáticas. A solução mais promissora em materiais de baixa densidade são os compósitos termoplásticos, que são o objeto deste trabalho.

A eficiência de blindagem de interferências eletromagnéticas foi estudada numa gama de 10 MHz até 6 GHz para sete compósitos termoplásitcos injetados comerciais sendo que a performance foi melhor nos materiais com fibras de carbono revistidas a níquel. A resistividade elétrica volumétrica também foi medida, na qual se destacaram materiais com fibras de carbono e matriz polimérica de PBT. A resistividade superficial foi medida através da técnia de quatro-pontas para duas direções: paralela e perpendicular à direção de injeção. Foi também medida a resistência através da impedância para três materiais (A, B e C). Estes três materiais foram escolhidos com base na combinação das suas propriedades, e com o intuito de melhorar a sua resistividade superficial e o contacto elétrico. Para isso foram utilizadas técnicas de pós-processamento como ablação laser e deposição de filmes metálicos. A ablação da superfície com laser foi realizada em três materiais (A, B e C), que apresentaram dos melhores resultados de blindagem electromagnética, sendo os resultados idênticos àqueles obtidos para as amostras sem ablação no caso da resistividade. O métodos das impedâncias foi utilizado para medir a resistência destes três materiais antes e depois da ablação a laser para calcular a sua resistividade. O material A e C apresentaram uma redução na resistividade. Por fim, uma deposição de um filme metálico de cobre foi aplicada a estes três materiais. O resultado da aplicação deste filme foi um aumento na resistividade volumétrica. Foi medida novamente a resistência para o Material A através da impedância o que resultou numa redução da resitivdade elétrica.

Este trabalho demonstra que é possível encontrar termoplásticos compósitos com fibras de carbono, que conseguem cumprir os requisitos da indústria automóvel, sendo uma solução viável para substituir os metais apresentando densidades menores.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source



5th of July 2021

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Notation and Glossary

ρ	Electrical resistivity	Ω·cm
σ	Electrical conductivity	$S\cdot cm^{-1}$
R	Resistance	Ω
A	Cross-sectional area perpendicular flow of electricity	cm^2
l	Distance between the electrodes	cm
R'	Electrical resistance	Ω
R''	Electrical Reactance	Ω

Greek Letters

σ	Single bond
π	Double bond

Indexes

T	Transmitted
I	Incident

List of Acronyms

ESD	Eletrostatic Discharge
EMC	Eletromagnetic Compatibility
EMI	Eletromagnetic Interference
ICPs	Intrinsically Conductive Polymers
CPCs	Conductive Polymer Composites
GHG	Greenhouse Gas
EM	Eletromagnetic
EMW	Eletromagnetic Waves
SE	Shielding Effectiveness
dB	Decibel
P	Power
E	Energy Field
H	Magnetic field
HOMO	Highest occupied Molecular Orbital
LUMO	Lowest unoccupied Molecular Orbital
PANI	Polyaniline
PPy	Polypyrrole
PTH	Polythiophene
PPP	Polyparaphenylne
PPV	Poly(p-phenylene vinylene
PEDOT	Poly(3,4-ethylenedioxythiphene)
PF	Polyfuran
PC	Polycarbonate
PA	Polyamide
PVDF	Poly(vinylidene fluoride)
PP	Polypropylene
PMMA	Poly(methylmethacrylate)
PVA	Poly(vinylalcohol)
PE	Polyethylene
PBT	Polybutylene terephthalate
CB	Carbon Black
CF	Carbon Fibre
CNF	Carbon Nanofibers

GO	Graphene Oxide
CNT	Carbon Nanotubes
SWCNT	Single-Walled Carbon Nanotubes
MWCNT	Multi-Walled Carbon Nanotubes
PCBs	Printed Circuit Boards
VNA	Vector Network Analyser
OCP	Open-Circuit Voltage
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
SED	Secondary Electron Detector

1 Introduction

1.1 Framing and presentation of the work

Automotive manufacturers have been investing time and resources to reduce the weight of their final product having in mind fuel consumption and cost reduction. Accordingly, there is an increasing interest by the automotive industry in replacing the high-density parts, namely metallic ones, with lower density materials at a competitive cost, without compromising the final quality and performance of the product. Electronic housings are one of the parts that the replacement of metal is being studied. Nonetheless, these electronic enclosures must guarantee electromagnetic compatibility with other electronic devices that are placed in the surroundings. EMC is tested in automotive parts from radios to engines. In general, to be electromagnetically compatible, electromagnetic interference must be shielded, and enough electrical conductivity must be assured in the enclosure. Thus, it is of the utmost importance that the new material displays similar performance as provided by the metal ones.

Engineering polymers are the most promising materials due to their high versatility and low density. In fact, polymers have the great advantage of being easily modified to achieve the desired properties. To be applied in the automotive industry, the most common physical properties that plastic-based materials need to have are thermal conductivity, electrical conductivity, and mechanical strength combined with their processability(1). These properties can be highly improved by using fillers dispersed in the polymer matrix. Several types of fillers can provide such properties as metallic or carbon-based ones. Nevertheless, the filler orientation, distribution, and compatibility with the polymer matrix are critical parameters that may influence electrical conductivity. The filler orientation highly depends on the processing parameters, for example, in the plastic injection moulding process(2). Matrix compatibility can be improved by filler functionalization, for example, by polymer wrapping (3).

The type of material used in electronic enclosures plays a crucial role in their electromagnetic compatibility (EMC). Still, another important variable is the design, mainly in what concerns the printed circuit boards, cables, and the enclosure itself.

Strategies for improving electrical conductivity and consequently EMC performance are currently being studied(4). These include removing the insulating skin layers of injected polymers by laser ablation and applying metallic coatings on the surface to promote electric contact between parts by reducing the surface resistivity.

The present dissertations aim at contributing on the characterization of the electrical conductivity and electromagnetic interference shielding effectiveness of commercial materials, comparing them to each other and analysing their potential on replacing metals in electronic enclosures. The viability of laser ablation and metallic coatings on said materials to improve electrical conductivity is also studied.

1.2 Presentation of the company

Bosch Car Multimedia Portugal, S.A in Braga focus on the development and production of solutions for infotainment systems and security sensors for automotive industry. The company is one of the largest exporters in Portugal providing to approximately 50 automotive manufacturers over Europe and is also one of the highest employing corporations in the location.

1.3 Contribution of the author to the work

In this work I performed an extensive research of the polymeric materials available to be used in electronic applications capable of shielding electromagnetic interference while being electrically conductive. After selecting several commercial injected thermoplastic composites, I performed the measurements of electrical resistivity and electromagnetic interference shielding effectiveness of seven different materials. The step that followed was testing laser ablation parameters to determine which ones would provide better results by analysing the surface in the scanning electron microscope. After determining the best conditions, I measured the electrical resistivity for three selected materials. After that, said materials were coated with copper for me to measure the electrical resistivity again.

1.4 Organization of the dissertation

The first chapter introduces the motivation of this work by briefly describing the need for automotive manufacturers to reduce weight by changing to lower density materials while maintaining performance. This chapter presents the most promising materials, and the strategies pursued to further improve their electrical conductivity. The critical aspects to be considered when designing electronic enclosures are also introduced. Lastly, a brief presentation of the company is given.

The second chapter states why automotive manufacturers want to change for lower density materials, followed by the concepts and importance of electromagnetic compatibility (EMC) and electromagnetic interference (EMI) shielding. The state of the art of materials that are currently being studied for EMI shielding is presented. This chapter also describes the main advantages of using engineering polymers over metals and introduces the intrinsically conductive polymers (ICPs) and conductive polymer composites (CPCs). Concepts as filler functionalization, anisotropic behaviour, and the influence of the processing parameters in the fillers alignment and distribution is briefly described. Some aspects to have in mind when designing electronic applications are described which include printed circuit boards, cables, and enclosures. Lastly, some post-processing techniques like laser ablation and metallic coatings are briefly analysed to improve electrical conductivity in the contact between parts.

Chapter 3 presents the commercial injected thermoplastic composites to be studied and the methods used to characterize them. Said methods include measurement of electromagnetic interference shielding effectiveness, electrical resistivity through four-point technique and impedance, surface removal by laser ablation, morphology analyses by scanning electron microscopy and application of metallic coating by sputtering.

The results obtained on the electrical resistivity and electromagnetic interference shielding measurements of the studied materials are presented and discussed in Chapter 4.

In Chapter 5, all the conclusions relating to this work are presented. Chapter 6 follows with an assessment of the work developed in this dissertation.

2 Context and State of the art

2.1 Automotive electronic applications

Automotive industry for years used mainly metals in vehicles due to their excellent properties and the lack of better options at the time. Despite their remarkable performance, metals could be expensive and heavy. Automotive manufacturers are facing stricter environmental regulations, and consumers are more and more interested in affordable, lightweight, and fuel-efficient vehicles. Since lightweight vehicles directly influence the fuel-efficiency, materials with lower densities than metals need to take a more prominent role in the constitution of the automobile(5). For example, a 10 % reduction in weight results in a 5 % to 7 % reduction in fuel usage(6), which plays a strategic role in increasing energy efficiency. In addition, low fuel consumption accounts for low greenhouse gas (GHG) emissions, and with the price of fuel continuously rising, it is critical to find solutions to produce lightweight vehicles(7)(8). Although weight is undoubtedly a key criterion, the cost is the most important decision factor when talking about a market-driven industry. Thus, the materials used by the manufacturers must be cost-competitive, but the time to market should also be appealing. These new materials need to perform on the level of metals or better, which means that they must comply with some requirements. For electronic applications, electromagnetic compatibility must be achieved, and for that, electromagnetic interference must be shielded(9).

2.2 Electromagnetic Compatibility: Concepts and Importance

In the early days of electronic devices, there was no control over electromagnetic interference (EMI), which caused equipment to interfere with each other. With the rapid growth of electronic technology, more and more devices started to be used, like mobile phones, wireless devices, televisions, and many other types of electronic equipment(10). For those devices to perform well, controlling the electromagnetic environment is a key requirement to achieve it, preserving their integrity and functionality. The ability of electrical equipment or system to properly work in the involving electromagnetic environment, without impairing their functions and without faults and vice versa, is called electromagnetic compatibility (EMC)(9)(11).

An electromagnetically compatible system should not cause interference with other systems or with itself, and it should not be susceptible to emissions from other systems. EMC directives like Directive 2014/30/EU from the European Commission were created to ensure equipment compatibility. Although EMC standards could differ from country to country (or union of countries), the manufacturers are obliged to provide those proving that their products were tested and met the requirements of the country. Electromagnetic emissions are controlled so as not to disturb other equipment, and the equipment’s immunity is also regulated not to be influenced by other electronic devices(11). Accordingly, emission relates to the generation of unwanted electromagnetic energy and needs to be reduced below certain levels to not cause disruptions in other systems. On the other hand, immunity is the capability of a system to perform even in the presence of electromagnetic interferences. The electromagnetic interference (EMI) is reduced using shielding mechanisms.

2.2.1 Electromagnetic Interference Shielding

Electromagnetic interference (EMI) is defined as the signals emitted by electrical circuits during its operation which can disrupt the proper operation of electronic devices in the vicinity or cause damage to living or biological species(12). There are different ways that EMI can be transferred from a source to the affected device: radiation, conduction, or induction (13). However, radiated and conducted are the main types of interference depending on the source and its path of transmission. Radiated interference is normally originated in an external device/source and travels through air, whereas conductive interference relates to the radiation created internally in a device that propagates through power or signal conductors (1).To minimize EMI a material is normally placed between the source and the device working as a shield. These barriers attenuate electromagnetic waves in three different ways: reflection, absorption, and multiple internal reflections, as schematized in Figure 1. The main mechanism of shielding is the reflection in which the barrier must have mobile charge carriers (electrons and holes) capable of interacting with electromagnetic (EM) radiation and attenuate it. Materials whose main mechanism of shielding is reflection are distinguished for their excellent electrical conductivity, like metals, due to the presence of free electrons (13). However, high conductivity is not required for shielding because conduction requires connectivity in the conduction path, whereas shielding does not (14). The second most important mechanism of shielding is absorption, and it relies on the interaction of the electric and/or magnetic dipoles of the material with the electromagnetic waves. The shielding effect through absorption normally increases with thickness and enhancement of electric/magnetic dipoles(15). The last shielding mechanism is multiple reflections on the interior of the material, benefiting from larger surface area materials like foams(15). This type of shielding is usually inconsequential since most electromagnetic waves (EMW) are reflected on the exterior surface(16).

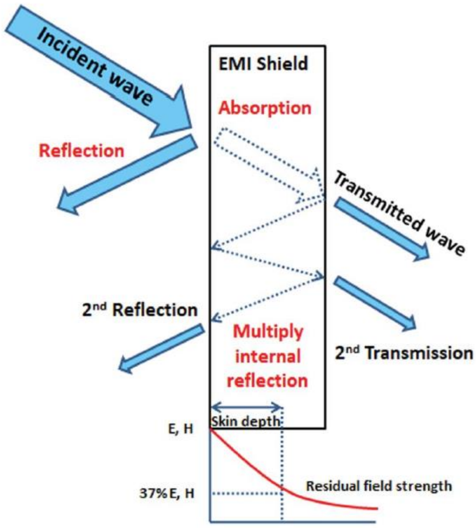

Figure 1.EMI Shielding Mechanisms: Reflection, absorption and multiple reflections [extracted from (15)*].*

The shielding ability is usually quantified by the shielding effectiveness (*SE*) parameter. The total shielding effectiveness is given by the sum of all the mechanisms involved according to Schelkunoff's equations as follow:

$$SE_T = SE_R + SE_A + SE_{MR} \quad (1)$$

where SE_T is the total shielding effectiveness, SE_R, SE_A, and SE_{MR} represent the shielding efficiencies due to reflection, absorption, and multiple reflections, respectively. Shielding efficiency is generally expressed in decibel (dB) and as stated in the literature "shielding efficiency is given by the ratio of the incident radiation power to the transmitted power" which can be calculated based on the power (*P*), energy field (*E*) or magnetic field (*H*) ratios(1,15,16):

$$SE = 10log\frac{P_T}{P_I} = 20log\frac{E_T}{E_I} = 20log\frac{H_T}{H_I} \quad (2)$$

where P_I, E_I, and H_I represent the incident power, the electric field, and the magnetic field, respectively. P_T, E_T, and H_T represent the transmitted power, the electric field, and the magnetic field, respectively. The energy transmitted through the shielding material is as less as higher the dB levels of EMI SE are(1). For most common applications, a shielding efficiency of 30 dB is recommended for commercial applications, which means that 99.9 % of the incident radiation is blocked. However, 40 dB is normally the required value for electronic housings(10)(1).

2.3 Materials for Electromagnetic Interference Shielding

EMI shielding relied mainly on metallic and magnetic materials, which could offer high shielding effectiveness (SE). Metals like steel, copper, aluminium and iron are often used for shielding purposes due to their high electrical conductivity and magnetic permeability(1). However, the recent technology growth has boosted the search for alternatives capable of replacing metals with other materials with better performances(17)(18).

Research has been focused on polymer-based materials since they could perform as good as metals and may also have some advantages over these. In this direction, conducting polymers (ICPs) have attracted the attention of researchers since they have excellent electrical conductivity, which can be further improved with chemical doping(1,19). Insulating polymers have also been studied as EMI shielding material, although they are only applicable with the introduction of electrically conducting fillers into the polymer matrix, originating conductive polymer composites (CPCs)(1).

2.3.1 Thermoplastics pros and cons

In the automotive industry, it is clear that metals should be replaced in some parts of the manufacturing process; alternatives were and are still being studied to this end. The leading solution is the use of engineering polymers since they offer several advantages over metals(1).

As mentioned, polymers offer variety and versatility for every application since many engineered polymeric materials have different properties and can be blended for some specific application.

Polymers are generally divided into two big categories of materials based on their thermal properties: thermoplastics and thermosets, which differ in their structure and how they react to heat(20,21). Thermoplastics have a simple molecular structure comprising chemically independent macromolecules(20) - Figure 2 (left). Thermoplastic is characterized by the ability to be moulded at high temperatures(20). On the other hand, thermosets have a more complex molecular structure being three dimensional and chemically cross-linked - Figure 2 (right). As a result, thermosets are not affected by heat after the hardening or curing process(21).

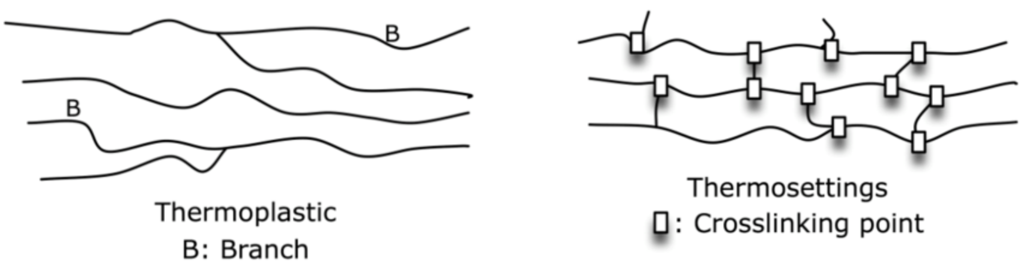

Figure 2. Schematic representation of thermoplastic and thermoset structures. [Extracted from (22)*].*

As mentioned before, the automotive industry is one of the biggest consumers of thermoplastics, and this is related to the excellent features that these offer over metals(20):

- Lightweight compared to metals without compromising structural strength:
    - Better car performance and reduced fuel consumption;
    - Easier to handle products and reduced shipping costs.
- More design freedom and lower manufacturing times;
- Corrosion resistance;
- Higher flexibility and ability to produce more complex parts.

Despite every positive aspect of polymers, most of them are not inherently adequate for electronic applications due to their insulating properties in opposition to the conductive nature of metals. However, this setback can be overcome by using additives that can enhance the properties of the material and even make them electrically conductive. Conducting polymers can also be used for EMI shielding due to their excellent electrical conductivity in doped states.

2.3.2 Intrinsically Conductive Polymers

Intrinsically conducting polymers (ICPs) are known as synthetic “metals” due to their electrical, magnetic, and optical properties being identical to those of metals and semiconductors(19).

Intrinsically conductive polymers present alternating single(σ) and double(π) bonds, as it can be seen in Figure 3, and when π-electrons are present, these polymers get their electrical properties(15). The p-orbitals overlap in the π bonds, giving mobility to electrons to delocalize between carbon atoms, being able to move along the polymer chain(23).

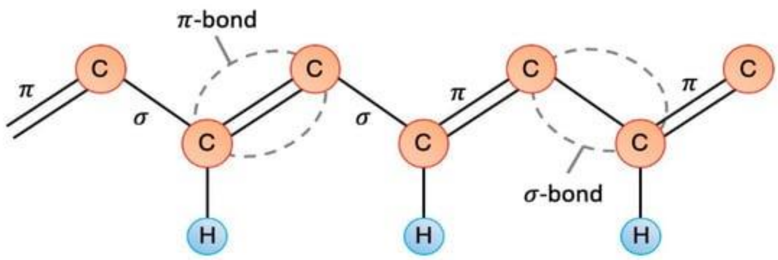

Figure 3. Structure of a conjugated backbone of an intrinsic conductive polymer (ICP) [extracted from (23)*].*

There are two energy levels with this electronic configuration: valence band or the highest occupied molecular orbital (HOMO) and the conducting band, also known as lowest unoccupied molecular orbital (LUMO). HOMO at lower energy can give the electrons, while LUMO at higher energy can attract the electrons(19).

Bond attraction causes the formation of an energy gap, also called band-gap, which determines if the material is an insulator, semiconductor, or conductor. The π-electrons present in the backbone can jump into the conduction band by excitation(24). This movement from the valence band to the conduction band can be induced by applying an electric or magnetic field and originates the conduction mechanism. Smaller energy gap between the two bands means easier conduction.

To overcome the energy gap created, dopant ions are incorporated into the structure. The dopant ions are added to the structure to withdraw electrons from the polymer chains and add electrons to the polymer backbone. These dopant ions suffer from redox processes giving place to the creation of charge carriers in the form of polarons (radical ions), bipolarons (dications or dianions) and solitons(25), as shown in Figure 4.

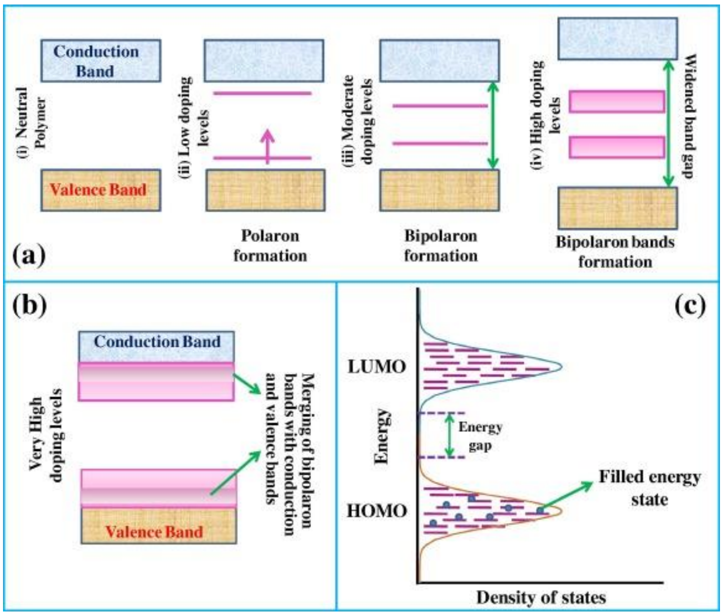

Figure 4. (a) Formation of polaron, bipolaron and bipolaron bands as a function of doping for ICPs; (b) Merging of bipolaron bands with conduction and valence bands at very high doping levels; (c) Gaussian distribution of localized states in HOMO and LUMO orbitals of ICPs [extracted from (25)*].*

On this type of polymers, ICPs, parameters like doping level, dopant ion size, oxidation state, protonation level, morphology and chemical structure can be adjusted to achieve desired levels of electrical conductivity, which makes them suitable for EMI shielding applications(15). Additionally, mobile charges (polarons, bipolarons, and solitons) and bond charges (dipoles) at the polymer backbone define the shielding efficiency of ICPs.

The most studied and used conductive polymers are polyaniline (PANI) and polypyrrole (PPy) due to their excellent stability (1). Other polymers are also used, and this includes polythiophene (PTH), polyacetylene, polyparaphenylene (PPP), poly(p-phenylene vinylene) (PPV), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyfuran (PF).

When undoped, these polymers exhibit poor conducting characteristics within the semiconductive or insulating range (10^{-10} to 10^{-5} $S \cdot cm^{-1}$), but when in doped states, these materials can be in the semiconductive or metallic range (up to 10^{5} $S.cm^{-1}$)(15).

2.3.3 Conductive Polymer Composites

With the addition of electrically conductive fillers, insulating polymers are also used for EMI shielding. A conductive network of fillers is required for EMI shielding applications(26). These polymeric composites are used due to their lightweight, flexibility, stability, chemical resistance, and easy processing(15). The different types of fillers that can be used to improve the conducting properties of these polymers can have several forms and shapes, such as particles, fibres, flakes, sheets, or tubes. These fillers can be metallic, magnetic, carbonaceous, or another inorganic material(1). The most used polymers are polystyrene (PS), polycarbonate (PC), polyamide (PA), poly(vinylidene fluoride) (PVDF), polypropylene (PP), poly(methylmethacrylate) (PMMA), poly(vinylalcohol) (PVA), polyethylene (PE) and polybutylene terephthalate (PBT).

2.3.3.1 Metallic fillers

Metals have excellent electrical conductivity, which makes metallic filler-based polymer composites an excellent option for EMI shielding. The shielding mechanism that is characteristic of metals is reflection of the electromagnetic radiation. The latter is due to the free electrons, but reflection might be unwanted in some cases because of the secondary electromagnetic radiation effect(15). Reflection is predominant at lower frequencies so metals present higher shielding efficiency in that range which decreases with the increase in frequency(15).

Normally metals are used as thin layers deposited on the surface, powdery fillers, fibres, and alloys, and can even be used in combination with other fillers like carbon-based ones. The metals mostly used as fillers are copper, silver, aluminium, steel, nickel, cobalt, iron, brass, or tin(1,15). The electrical conductivity of some metals is presented in Table 1.

Although metals seem ideal for EMI shielding due to their high electrical conductivity, they have a few drawbacks like the difference in density, poor dispersion in the polymeric matrix, and decreased processability. Nonetheless, the major drawbacks are the oxidation of the metallic particles present in the polymeric matrix into metal oxides which decreases the electrical conductivity of the composites and the higher density compared to carbon-based fillers(18).

Table 1. Electrical conductivity of some metals [adapted from (15)*].*

Metals	Conductivity ($S{\cdot}m^{-1}$)
Silver	$6,3 \times 10^7$
Copper	$5,9 \times 10^7$
Gold	$4,5 \times 10^7$
Aluminium	$3,8 \times 10^7$
Cobalt	$1,6 \times 10^7$
Brass	$1,6 \times 10^7$
Nickel	$1,4 \times 10^7$
Iron	$1,0 \times 10^7$
Tin	$8,7 \times 10^6$
Steel	$6,2 \times 10^6$
Lead	$8,4 \times 10^6$

2.3.3.2 Carbon-based fillers

Carbon-based fillers are amongst the most used in polymeric matrices for EMI shielding since they show excellent electrical conductivity, low density, good physical properties and high mechanical, chemical and thermal stability(15). These fillers serve not only to improve the electrical properties of the material, but they can also reinforce the mechanical properties. The more conventional carbon-based fillers are carbon black (CB), graphite, graphene, carbon fibre (CF) and carbon nanofibers (CNF), and carbon nanotubes (single-walled, SWCNT, or multi-walled, MWCNT)(1).

Carbon-black

Carbon-black is usually obtained by partial combustion or thermal decomposition of hydrocarbons, and it consists of carbon particles fused into aggregates (Figure 5). Carbon-black is extensively used in rubber products due to its affordability, easy production, and physical properties enhancement. In plastics, CB is mainly used to protect against UV radiation, as mechanical reinforcement, and improve its electrical conductivity (15)(18). The structure of carbon-black depends highly on the manufacturing and processing conditions. The typical electrical resistivity of CB is 10^{-2} - 10^{-3} $\Omega{\cdot}cm$ and may vary depending on the morphology, preparation conditions and particle size. CB with high surface area and high degree of branching promotes better contact impacting positively the conductivity.

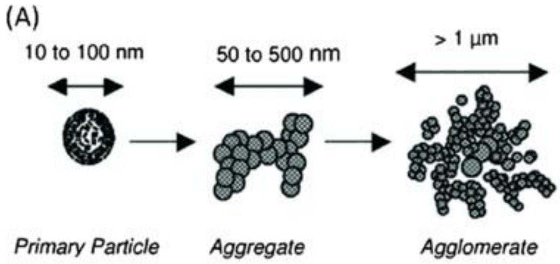

Figure 5. Structure of carbon black [adapted from (27)*].*

Al-Saleh and Sundararaj(28), in 2013, studied the effect of filler concentration from 1 % to 10 %vol to determine the percolation threshold value. The shield thickness was also studied to observe the behaviour of the SE. The percolation threshold observed was 2.5%vol and the best SE was 42.7 dB at 10 %vol with a 2.8 mm thick polypropylene (PP)-based carbon black composite.

Graphite and graphene

Graphite is a crystalline material in which sheets of carbon atoms arranged in hexagonal rings are stacked parallel to one another (Figure 6 – a). Graphite is soft and brittle due to weak van der Waals interactions between the sheets. The carbon atoms are connected through covalent carbon-carbon bonds(15). What makes graphite an attractive filler is its low price, good electrical conductivity, and mechanical and thermal stability.

Panwar et al.(29), in 2010, studied a polypropylene(PP)-based graphite composite on the radio frequency ranges observing a maximum of 44.12 dB of SE at 2.76 GHz.

Graphene is a two-dimensional sheet of carbon atoms bonded to each other organized in the form of hexagonal rings(18) (Figure 6 - b). Graphene has ultrahigh specific surface area and for that the percolation threshold can be achieved with low levels of filler concentration(15). Graphene emerged as one of the most promising fillers for EMI shielding due to its excellent electrical and thermal conductivity, excellent charge carrier mobility and unique mechanical, optical, and magnetic properties(1). However, the lack of surface functionalities can be detrimental for EMI absorption creating mismatching impedance between material and air(15). Thus, and as an alternative, graphene derivatives such as graphene oxide (GO) are used.

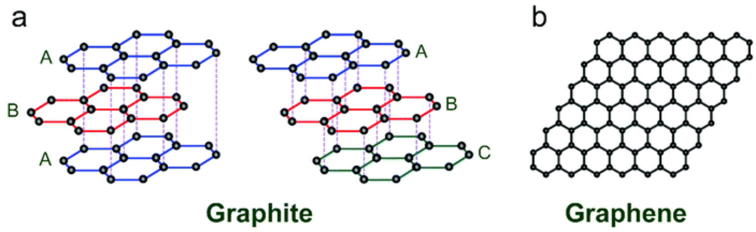

Figure 6. Structure of a) Graphite and b) Graphene [extracted from (30)*].*

Carbon Fibre

Carbon Fibre (CF) is a pure form of carbon, containing more than 90 wt% of carbon in which the atoms are arranged in hexagonal rings and are aligned with the fibre length axis as seen in Figure 7. CFs can be obtained through pyrolysis of materials like polyacrylonitrile (PAN)(18). Besides PAN CFs there is also Pitch CFs that can be obtained as a secondary product of petroleum or from the pyrolysis of polyvinylchloride(31). Interest in carbon fibres is related to their high mechanical strength, low weight, and high electrical conductivity(1).

Jou et al. (32), in 2001, studied the SE of different lengths of carbon fibre in nylon-66 based composites obtaining better results for longer CF. For a range up to 1500 MHz the SE varied between 45 to 75 dB with 30 wt% long CF composite(33).

Carbon nanofibers (CNF) differ in size from carbon fibres since CNFs are formed by shapes like cups, cones, or plates with diameters on the scale of 50 nm to 300 nm also being hollow fibres(18). CNF can be synthetized through several chemical vapor deposition processes(20). CNFs combine aspects like mechanical strength, excellent electrical and thermal conductivities, large specific surface area, low density, among other properties, making them ideal fillers for EMI shielding applications(15). Carbon fibres and nanofibers are also applied to reinforce polymer composites used in automotive structural components since they have lower densities than metals and can display higher mechanical strength.

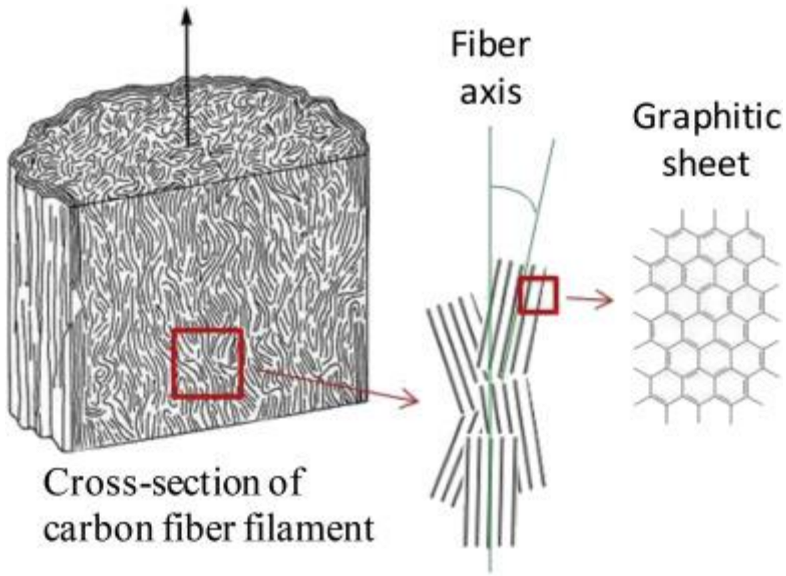

Figure 7. Representation of the alignment of graphitic sheets in carbon fibres [extracted from (34)*].*

Carbon nanotubes

Carbon nanotubes (CNT) are hollow tubes or cylinders made of hexagonal carbon rings being basically rolled up graphene sheets. CNTs range of applications is broad, but mainly they are used as additives to improve mechanical and electrical properties of materials(18). Carbon nanotubes can be divided into single-walled nanotubes (SWCNT) (Figure 8 - (left)) and multi-walled nanotubes (MWCNT) (Figure 8 - (right)), differing in their electrical properties. The electrical properties differences of these two categories of CNTs relies on the diameter and aspect ratio of the nanotubes, exhibiting different EMI shielding characteristic when added to the polymer matrix.(15). CNTs have several advantages relating to other conventional fillers, like attaining high EMI shielding efficiencies at lower loadings levels due to the easy percolation of CNTs and excellent electrical conductivity(18). They also show great mechanical strength being up to now the most robust material known when talking about tensile strength(15). The diameter and length of the CNT are essential parameters to improve the dispersion in the polymer and the ability to form a conductive path.

MWCNTs present some advantages over SWCNTs for EMI shielding applications due to their lower cost, easier mass production and better thermal and chemical stability(1).

Yuen et al.(35), in 2008, studied the difference between *in situ* and *ex situ* polymerization method of MWCNTs in a PMMA matrix, having better performance for the *in situ* preparation. A SE of 32.06 dB was obtained as a maximum for a frequency of 2.18 GHz(35).

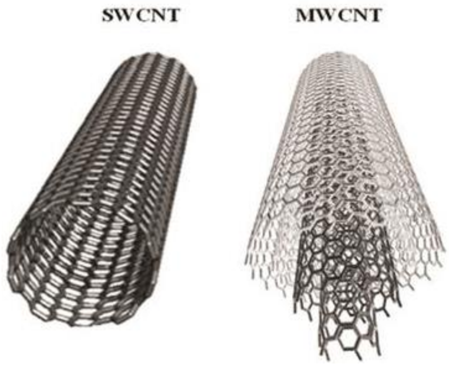

Figure 8. Structure of Carbon nanotubes [extracted from (36)*].*

2.3.3.3 Filler functionalization

Carbon-based fillers are often used as additives in polymeric matrices mainly due to their excellent properties and EMI shielding improvement of the material. However, they have a significant drawback: the filler dispersion and distribution in the polymer matrix. The latter occurs because this type of fillers tends to form agglomerates due to their strong interactions and van der Waals forces(3,37). Different strategies are used to solve the agglomeration problem, improving the filler dispersion via filler functionalization, which includes covalent modification (or chemical functionalization) and non-covalent modification (or physical functionalization) depending on the type of interactions(3).

Covalent functionalization

Covalent functionalization consists on the attachment of functional groups on the surface of the filler by covalent bonding(3,38). Chemical functionalization is normally achieved through oxidative processes (Figure 9). Despite being effective in promoting filler dispersion, covalent modification can cause deterioration of the properties of the particles, meaning that the electrical conductivity might decrease(38). For applications that require electrical conductivity covalent functionalization might not be appropriate, since the $\pi-\pi$ conjugation system which is responsible for the electrical conductivity is modified with the hybridization state changing from sp^2 to sp^3. For electronic applications non-covalent functionalization is of great interest(3).

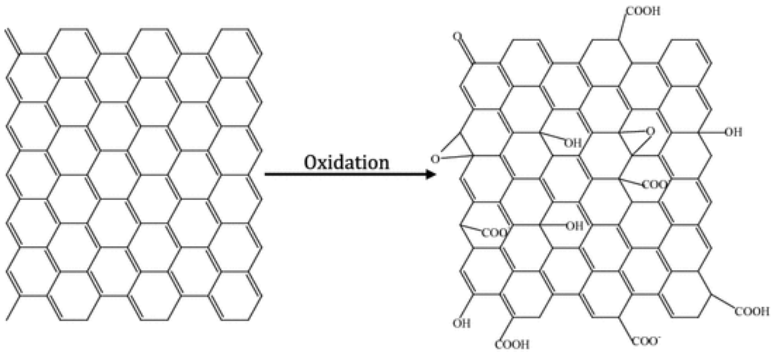

Figure 9. Schematic representation of the attachment of different functional groups after surface oxidation [extracted from (3)*].*

Non-covalent functionalization

The non-covalent mechanism is a non-destructive method that uses surfactants and polymer wrapping, where the intrinsic properties of the fillers remain untouched. This type of functionalization is achieved without chemical bonding. Instead, it relies on van der Waals forces and π-π interactions(3,38). Physical functionalization is normally carried out in three ways: polymer wrapping, surfactant adsorption and encapsulation – Figure 10.

In polymer wrapping, the polymer chain that is wrapped around the filler reduces the van der Walls interactions between fillers, thus increasing the dispersibility. For a polymer to be wrapped in a carbon filler, it must have a hydrophobic part to be compatible with the filler(3).

Surfactant adsorption is used for colloidal stabilization of carbon fillers, in which surfactants are adsorbed on the surface of the filler. The dispersibility is improved by keeping filler particles apart by electrostatic repulsion or steric hindrance, being that the repulsive forces are able to overcome the van der Waals interaction amongst the fillers(3).

Encapsulation is described as the introduction of a foreign material in the hollow cavity of the carbon material like carbon nanotubes. The foreign material is kept inside the CNT through van der Walls interactions(3).

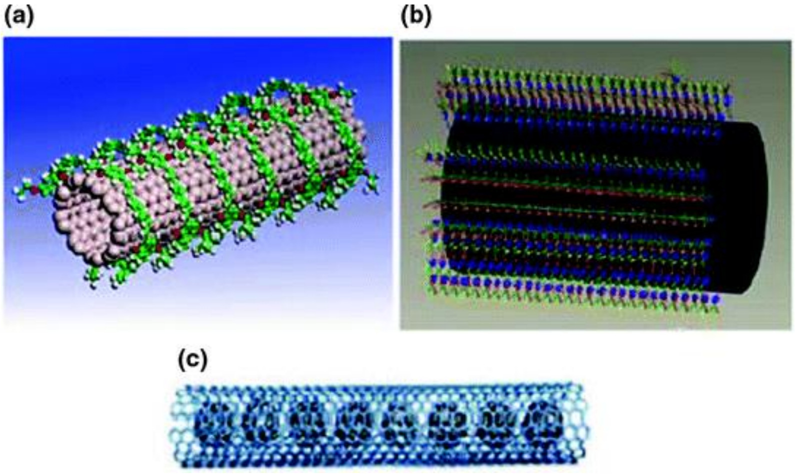

Figure 10. Representation of non-covalent functionalization: a) polymer wrapping, b) surfactant adsorption and c) encapsulation [extracted from (3)*].*

2.3.3.4 Anisotropy

The alignment of the fillers in the matrix plays a big part in the physical properties of the materials. The material can present anisotropy which is a property of the material in which it can exhibit directionally variable physical properties. Filler alignment induces anisotropic behaviour in the electrical conductivity of the composite, being that it behaves as a conductor only in a preferred direction(39).

Fillers themselves can present anisotropy due to their aspect ratio. For CNT and CF composites the electrical conductivity is heavily influenced by the orientation of the filles because of their high aspect ratio, while for CB this is close to 1 meaning that the electrical conductivity is expected to be isotropic(40). CNTs alignment in compression moulded plates (a) and in extruded films (b) are seen in Figure 11. CB isotropic behaviour is also represented in Figure 11(c).

Increased alignment of the fillers affects the interconnectivity which leads to an increase in the percolation threshold (volume percentage at which the percolating network is formed)(39).

Processing parameters of injection moulding highly influences the alignment of the fillers in the matrix possibly resulting in anisotropic behaviour.

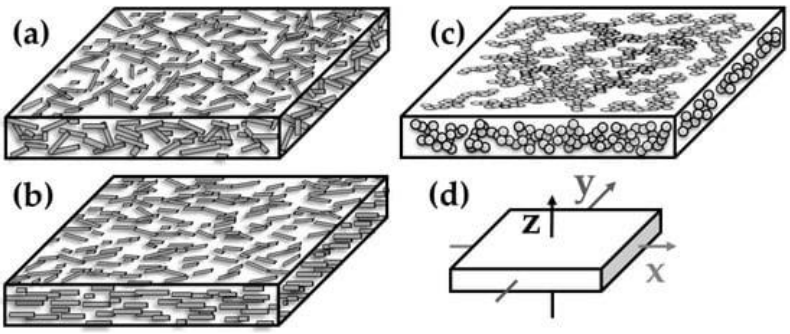

*Figure 11. Schemes of filler orientation: (**a**) CNTs in compression moulded plates, (**b**) CNTs in extruded films in extrusion direction x, (**c**) CB in plates and films, (**d**) measurement directions: z = through-plane; x = in-plane, parallel to the extrusion direction; y = in-plane, perpendicular to extrusion direction [extracted from* (40)*].*

2.3.3.5 Influence of the processing parameters on the filler orientation

One of the most used processes to produce conductive polymer composites is injection moulding since it is a cost-effective method to produce complex three-dimensional parts in a large scale, including electronic housings(2). Differences in the electrical conductivity of the composite are caused by changes in the conducting network induced by shear stress and heat. The amount of shear stress and heat induced into the composite are dependent on the processing parameters. The parameters that are most studied and seem to have a bigger influence in the conductivity of the composite are injection speed rate, melt temperature, mould temperature and holding pressure(41). Other aspect to have in mind is the filler content needed to ensure a conducting network. If not enough filler is present in the matrix to reach the percolation threshold, good electrical conductivity will not be achieved.

Filler Content

The amount of filler needed to create a conducting network is important and it's in fact influenced by some other parameters of the injection process itself. The filler content depends on the type of filler, mainly on their aspect ratio and on the arrangement of the filler in the matrix(2). Randomly organized fillers promote more contact between them which guarantees the movement of electrons, improving conductivity. When the fillers are more aligned and dispersed, more filler is needed to have the same conductivity. Particulated fillers need higher volume fraction than high aspect ratio fillers to ensure the same conducting network(41).

The filler dispersion and agglomeration should be a compromise between both aspects to ensure a good conducting network as seen in Figure 12 – c).

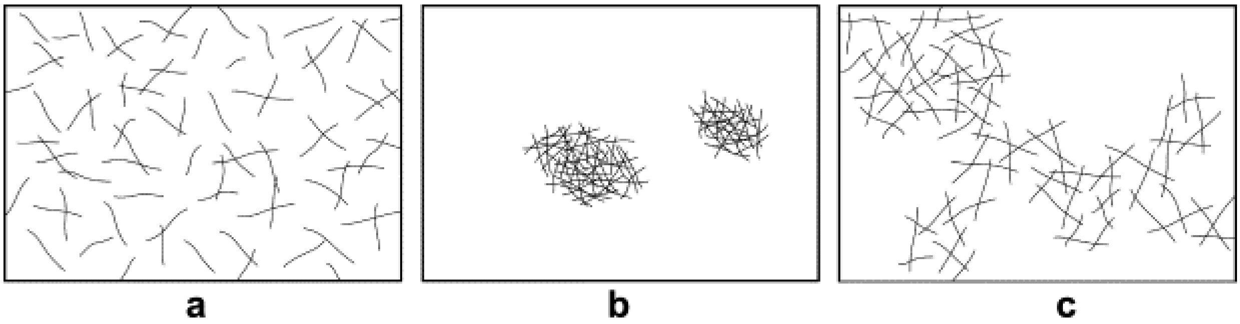

Figure 12. Dispersion and agglomeration of high aspect-ratio filler: a) dispersed; b) agglomerated; c) slightly agglomerated and disperse [extracted from (2)*].*

Injection rate

Injection rate is one of the parameters that has one of the most noticeable effects on the conductivity of the composite, being in fact a decrease of several orders of magnitude on the electrical conductivity(2). When the injection rate is increased, the flow shear becomes higher, and with it comes dispersive and orientative effects. The alignment of the particles results in a higher percolation threshold and anisotropic behaviour producing an overall decrease in conductivity(2,41). Due to high shear forces in the nozzle, high aspect ratio fillers like CF or CNT can experience shortening(41) while fillers like carbon black, in which the conductivity is achieved through aggregates of small particles, can suffer from disaggregation resulting in more disperse particles on the matrix with reduced contact between them(42).

Melt Temperature

Opposing to the injection rate, increase in melt temperature benefits the electrical conductivity. Higher temperature results in lower viscosity which leads to lower flow shear. The particles have more mobility to reorient themselves in the matrix resulting in a more randomly oriented conducting network due to more contact between fillers(2,41). The improvement in electrical conductivity is of some orders of magnitude.

Mould Temperature

The mould temperature does not influence as much as injection speed and melt temperature, but it has importance in lowering the surface resistivity of the material(41). When the melted fluid enters the mould, heat instantly starts to be transferred between both and a skin layer is formed by fast cooling on the surface(2). If the mould temperature is higher, then the cooling will be slower, and the skin layer will be thinner. Since the skin layer acts as insulating, the electrical conductivity is higher when the thickness is lower(43). This effect of the skin layer will be one of the parameters under attention of this thesis.

Holding Pressure

The processing parameter that influences the less is the packing pressure(41). The effect of this parameter is the rearrangement of the particles, creating a three-dimensional conducting network, resulting in more compact arrangement with more contact between fillers improving slightly the electrical conductivity. The increase of conductivity is lower for higher filler content(44).

2.4 Influence of the design in the Electromagnetic Compatibility of electronic parts

When designing for electronic protection and EMC many areas need to be addressed to optimize performance and ensure that the product operates without disruptions and without interfering with others. It is important to implement EMC from the start of the project, otherwise it might imply severe costs(1). The areas of attention when designing electronic products are usually related to the printed circuit boards (PCBs), cabling, and the enclosure itself that all together influence the EMC of the product(45).

2.4.1 Enclosures

The design of the electronic enclosure influences heavily EMI shielding with some important aspects being material, grounding, and apertures(46).

Firstly, the enclosure must be made of a conductive material, and it should keep those properties during the product life. When designing an electronic enclosure, one of the most important parts is the grounding because insufficient grounding may lead to earth loops, leading the electronic unit to radiate or pick up signals, resulting in poor EMC performance. Grounding is basically a path for a current to return to its source and should have low impedance and be as direct as possible(45).

Also important is apertures size, since for wavelengths equal to twice the opening, the shielding is heavily decreased. The aperture size for commercial products must be smaller than $\lambda/20$(45).

2.5 Electrical conductivity and electromagnetic compatibility performance improvement

Electrical conductivity in electronic enclosures must be achieved for excellent grounding and despite the conductivity of the material, sometimes between mating parts there is no connectivity due to bad contact. The lack of connectivity might be due to gaps where contact is not guaranteed, or the typical insulating skin layer of thermoplastic composites is present. To improve electrical conductivity between parts, conductive gaskets, metallic coatings, and laser ablation are some post-processing techniques used.

Conductive Gaskets

Conductive gaskets can be used to reduce the gap between panels. They are intended to be sandwiched between the mating surfaces to maintain conductivity and contact across the joint and ensure that the current is not deviated(45).

Metallic Coatings

Applying a metallic coating is a strategy to cover the surface of plastic enclosures. Several deposition methods can be used to this end, being the most common thermal spray, cold spray, evaporation, and sputtering(47).

Laser Ablation

One of the biggest issues with using injection moulded thermoplastic composites is that a skin layer that is “resin rich” is present on the surface with the fibres being underneath. This results in reduced conductivity on the surface(4). To expose the fibres, the skin layer can be removed with a laser. This technique is normally mentioned as laser ablation, in which conductive paths can be created, improving the overall conductivity, and thus reducing the resistivity of the surface(48)(4). Ablation is a combination of vaporization and melt expulsion of the polymer(49). The results of the laser ablation depend highly on the type of material and its properties like thermal conductivity, absorption coefficient and reflectance. Parameters such as power of the laser, mark speed, number of passes, and frequency influence the ablation(49).

3 Materials and Methods

3.1 Materials

Aiming to find alternative materials that could perform equal or even better than the metal-based ones currently used by the automotive industry in electronic housings, the first task was to find and select the most promising alternatives. Commercial injected thermoplastic composites were chosen, and it was decided to study the electromagnetic interference (EMI) shielding and the electrical resistivity in seven different materials that vary on their matrix, type of filler, and density accordingly to Table 2.

Table 2. Composition of the commercial materials including matrix, filler type, filler percentage and density.

Material	Matrix	Filler	Filler percentage (wt%)	Density (g/cm^3)
A	PBT	Carbon Fibre, Carbon Black	23 % and 10 %	1.36
B	PC	Nickel Coated Carbon Fibre	15%	1.31
C	PA66	Nickel-Coated Carbon Fibre	14 %	1.18
D	PA66	Carbon Fibre, Carbon Black	19.5 % and 7.5 %	1.23
E	PA6	Carbon Fibre, Steel Fibre, Graphite	11 %, 15 % and 11 %	1.51
F	PA6	Carbon Fibre, Graphite	15 % and 30%	1.41
G	PBT	Carbon Fibre	~20 %	1.38

All the commercial samples were prepared by injection moulding, and discs of 60 mm diameter and 2 mm of thickness were produced. According to the technical requirements of the characterization method, these discs were kept in this format or cut into smaller sizes and different shapes.

The specimens used to measure the superficial resistivity should have the dimensions of 10 mm × 20 mm × 2 mm (W x L x H). Whereas for measuring the volumetric resistivity, samples of 10 mm × 10 mm × 2 mm were used. These samples were cut from the large discs, as shown in Figure 13. For measuring the superficial resistivity, two pieces were cut (perpendicular and parallel to the injection flow) to determine the influence of the injection direction in electrical resistivity for these materials.

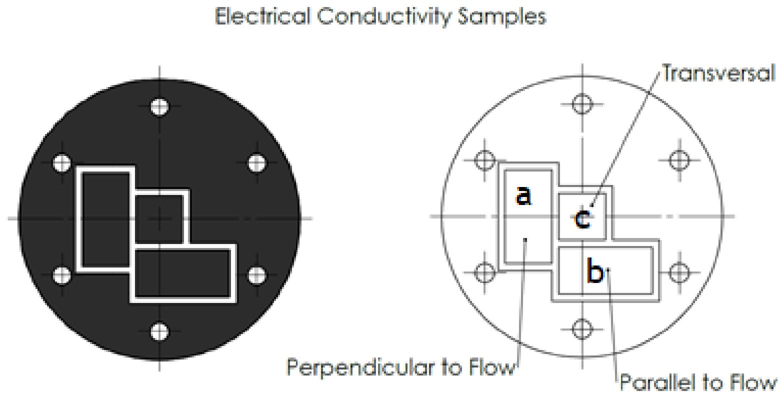

Figure 13. Specimens for electrical resistivity measurement: a) in-plane perpendicular direction; b) in-plane parallel direction; c) through-plane.

For measuring the electromagnetic interference (EMI) shielding effectiveness (SE), the complete disc samples were used according to Figure 14. For this study two types of samples were needed: a reference specimen and a load specimen, the difference being that the reference has no material in the place where the signal is going to travel between the flanges.

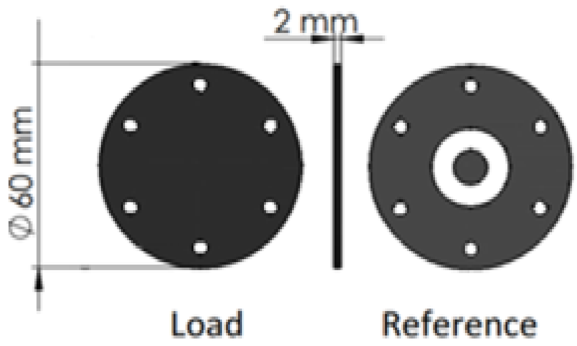

Figure 14. EMI shielding specimens: load and reference.

3.2 Electromagnetic Interference Shielding Effectiveness

EMI shielding is important to achieve in every electronic device; thus, shielding effectiveness needs to be measured to study the material's behaviour in the presence of electromagnetic interferences.

The experimental measurements were carried out according to ASTM D4935 standard, a test method for measuring EMI SE of planar specimens. The setup used for this measurement is shown in Figure 15.

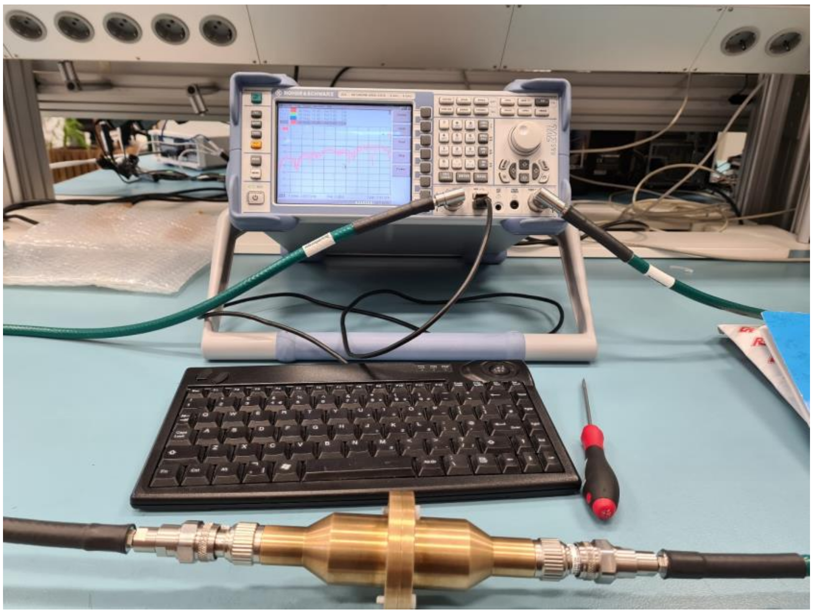

Figure 15. Setup for EMI SE measurement including VNA and specimen holder.

The setup is established by a vector network analyser (VNA) (Rohde & Schwarz ZVL6 2Ports) coupled with a coaxial specimen holder with internal and external conductors made of brass. An impedance of 50 Ω is maintained throughout the holder, and two attenuators of 10 dB are present at each end of it to insulate from input and output signals. This setup allows a range of frequencies to be measured from 10 MHz to 6 GHz.

The VNA is used to generate and receive radiofrequency signals, and to obtain the SE of the material the scatterings parameters are measured. The S_{21} parameter describes the electromagnetic power transmitted from port 1 (input port) to port 2 (output port) of the VNA.

The procedure starts by calibrating the VNA to measure the material samples. After calibration, two measurements are needed for each material. The specimens are placed between the two connectors and three screws were used to join both flanges. For the SE to be calculated, firstly the reference specimen is used to measure the incident signal since the space between the conductors is left open. Secondly, the reference specimen is switched with the load specimen and the measurement is repeated to obtain the received signal, this time with the sample between the conductors. Replicates of the load specimen were used for this measurement. Finally, SE can then be calculated according to equation (3):

$$SE|_{dB} = |S_{21}{}^{Load}|_{dB} - |S_{21}{}^{Ref}|_{dB} = 10log\frac{P_T{}^{Load}}{P_I} - 10log\frac{P_T{}^{Ref}}{P_I} = 10log\frac{P_T{}^{Load}}{P_T{}^{Ref}} \quad (3)$$

3.3 Electrical Resistivity

The electrical resistivity is an important property of a material since it indicates how much it resists to the flow of electric current. If a material presents low resistivity, it means that electricity flows easily in that material.

Electrical resistivity is the inverse of electrical conductivity, meaning lower resistivity gives higher conductivity.

$$\rho = \frac{1}{\sigma} \tag{4}$$

Resistance is given by Ohm's law:

$$R = \frac{V}{I} \tag{5}$$

Resistivity can be calculated by:

$$\rho = R \times \frac{A}{l} \tag{6}$$

being A the cross-sectional area perpendicular to the flow of electricity, and l is the distance between the electrodes.

Electrical resistivity can be measured in-plane known as superficial resistivity or through-plane known as bulk or volumetric resistivity.

The measurement of the electrical resistivity was based on the four-point technique, in which four cables are attached to the electrodes, being that the two on the edges get an applied current and the two in the middle measure the voltage drop in that specified length of the specimen. The applied current is measured with multimeter used as an ammeter (Keysight 34461A Digital Multimeter, 6 ½ Digit, Truevolt DMM) while the voltage drop is measured with a multimeter used as a voltmeter (Fluke 117 Multimeter).

An "homemade" device was used in which two different sets of electrodes can be assembled and switched to measure the desired resistivity – Figure 16 a). This set of electrodes was built based on the standard ASTM D4496-87 (Standard Test Method for DC Resistance or Conductance of Moderately Conductive Materials) and ASTM D257-07 (Standard Test Methods for DC Resistance or Conductance of Insulating Materials). One of these sets is used to measure the superficial resistivity – Figure 16 c) - while the other set is used to measure through-thickness resistivity – Figure 16 b). On the latter two electrodes are needed for the top and bottom.

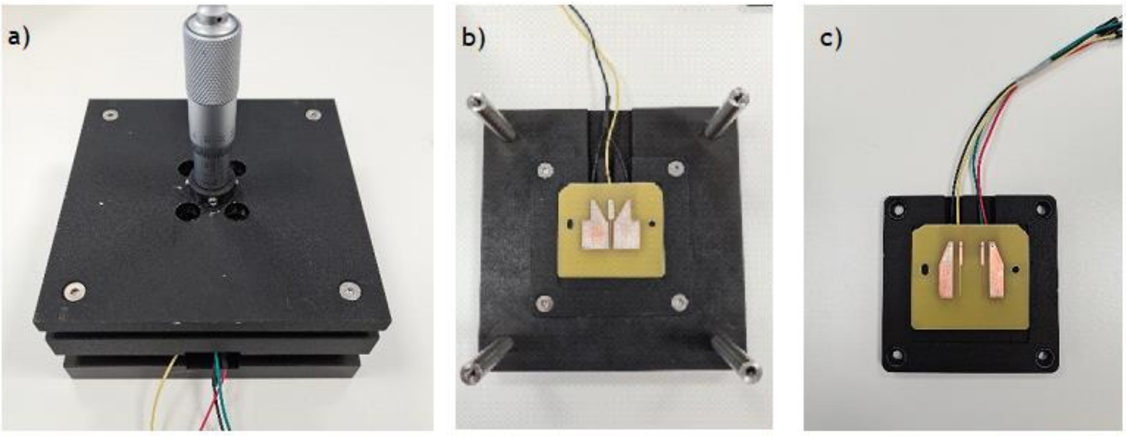

Figure 16. a) measuring device, b) volumetric resistivity electrodes, c) surface resistivity electrodes

For each material, five samples were tested for each direction. Three measurements for each sample were realized to have a more accurate result.

The sample is mounted in the right place contacting the electrodes and some adjustment with the micrometre can be made to guarantee a stable measurement signal. The cables are connected to the ammeter and the voltmeter respectively. After the contact pressure adjustment is done by the micrometre adjustment, the defined current is applied and maintained until its stable to read and register the voltage drop. The setup for electrical resistivity measurement is presented in Figure 17. With the intensity of the current and the voltage drop, the resistance can be calculated using equation (5). Knowing the dimensions of the specimen, the calculation of the resistivity can also be made using equation (6). Having the resistivity, conductivity can be obtained through equation (4).

The finalized setup is presented in Figure 17. The voltmeter is on the left, ammeter on the middle and on top is the power supply (Rohde & Schwarz HMC8043).

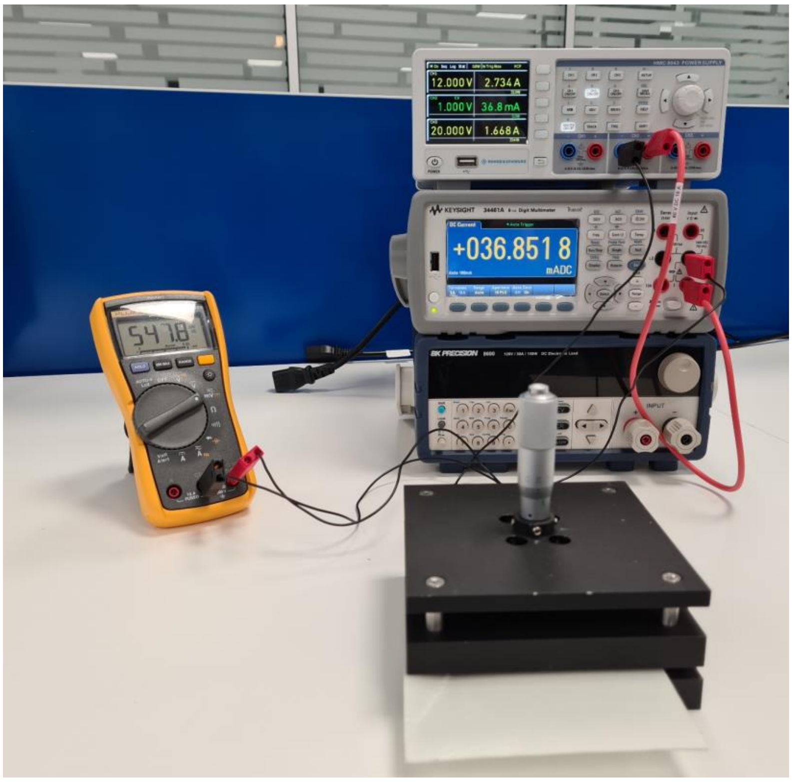

Figure 17. Electrical resistivity setup with multimeters (left and middle), measuring device (bottom) and power supply (top).

3.4 Impedance Measurements

Impedance measures the opposition that a material offers to the passage of current when a voltage is applied. Impedance is a complex number that includes a real part (*R'*, electrical resistance) and an imaginary part (*R''*, electrical reactance) with the same units as resistance.

This technique was used to measure the through-plane electrical resistivity, also known as bulk or volumetric resistivity, by determining how strongly the body of the material opposes the electric current to flow.

In Figure 18 it is presented the experimental setup developed to measure the impedance of the materials in a two-electrode configuration and evaluate their electrical behaviour. The experimental setup comprises a potentiostat/galvanostat with a frequency response analyser (Autolab PGSTAT302N) to generate and receive the signal, two copper electrodes (one for the bottom and one for the top) and a press machine to promote constant contact between the electrodes and the sample with 60 mm diameter. The impedance measurements were conducted at an open-circuit voltage (OCP) in the frequencies range of 0.1 Hz – 100 kHz. The electrical resistance was extracted from the Nyquist diagram obtained, and the resistivity is calculated according to Equation (6).

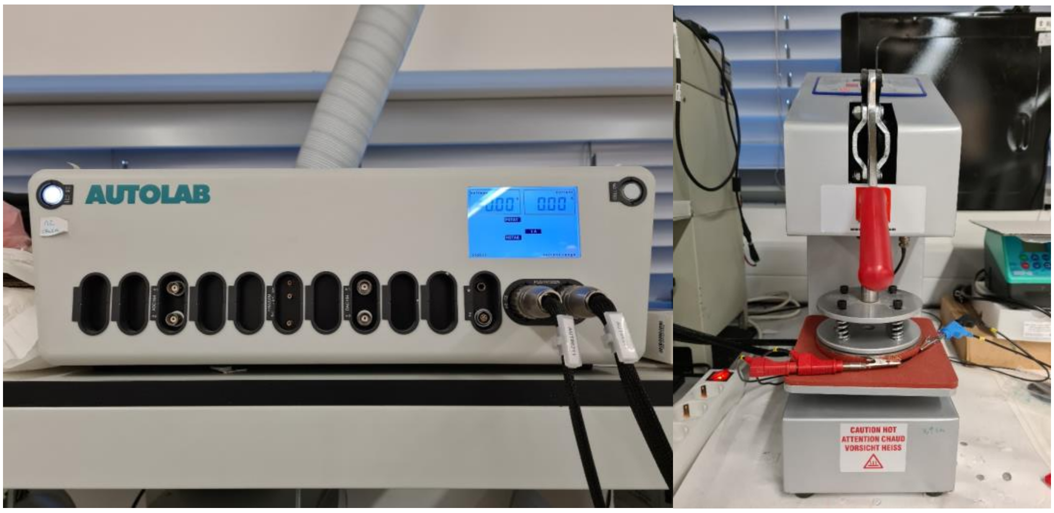

Figure 18. Impedance setup with potentiostat/galvanostat (left) and combination of press machine/electrodes (right).

3.5 Laser Ablation

Laser ablation consists on the irradiation of a solid surface with a laser beam resulting in the removal of material. This technique was used to remove the skin layer of injected polymers exposing the filler/fibres, improving the surface conductivity of the studied materials.

Equipment used in this dissertation is presented in Figure 19, and it includes a pulsed ultraviolet laser with a wavelength of 355 nm, having a maximum nominal power of 5 W, 40 kHz and 15 ns of pulse. A bidirectional filling scan was used with a step of 16 μm at a working distance of 194 mm. The laser beam is focused onto the material by a lens with a 160 mm focal distance, and the focal spot diameter is 16 μm. The experimental parameters of the laser to remove the surface layer of the studied samples are listed in Table 3.

Table 3. Parameters for laser ablation including power, frequency, mark speed and number of passes.

Material	Power (W)	Frequency (kHz)	Mark Speed (mm/s)	Nº of passes
A	4.5	20	1000	2
B, C	4.5	20	1000	3
C (discs)	4.5	20	500	2

Figure 19. Laser ablation setup at UPTEC.

The sample is then aligned in the ablation chamber and the chamber is closed. The laser ablation is started through the software installed in the associated computer.

3.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to observe the surface morphology of laser-ablated materials. The samples were placed on the sample holder using double-sided carbon tape. The microscope used to obtain these images was Phenom XL – Figure 20 - that is equipped with two detector systems: Energy dispersive spectroscopy (EDS) and secondary electron detector (SED). The latter is the one that allows for high resolution images of the surface.

To analyse the filler distribution throughout the matrix, cross-section was also performed. The samples were frozen and fractured in liquid nitrogen.

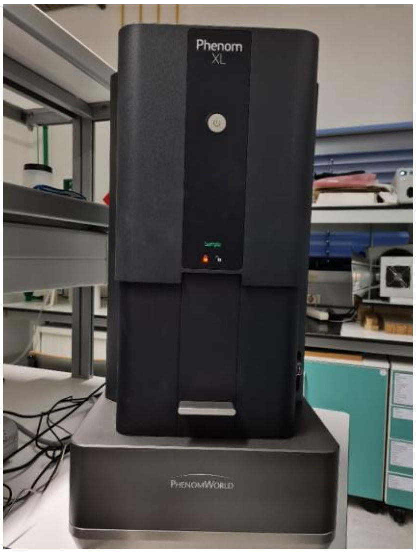

Figure 20. Scanning electron microscope (SEM) Phenom XL at ARCP/UPTEC.

3.7 Sputtering

Copper thin films (~1 μm) were deposited by DC magnetron sputtering, using the QPrep 400 Mantis ® Deposition system, at a power of 0.050 kW which considering that the Cu target has 10 cm diameter, corresponds to a power density of 0.64 W·cm^2. The base pressure and working pressure used were respectively ~1 x 10^{-6} mbar and ~5x10^{-3} mbar. The equipment used for this deposition is shown in Figure 21.

In this technique, atoms are vaporized from a metal target and deposited onto a substrate. The ejection of atoms is achieved with energetic particles that are generated due to voltage drop between the target and the substrate in the presence of an inert gas forming a gaseous plasma. The magnetron produces a strong electric and magnetic field that traps the charged particles close to the target promoting contact between them and the surface removing the metallic atoms which will eventually be deposited onto the substrate.

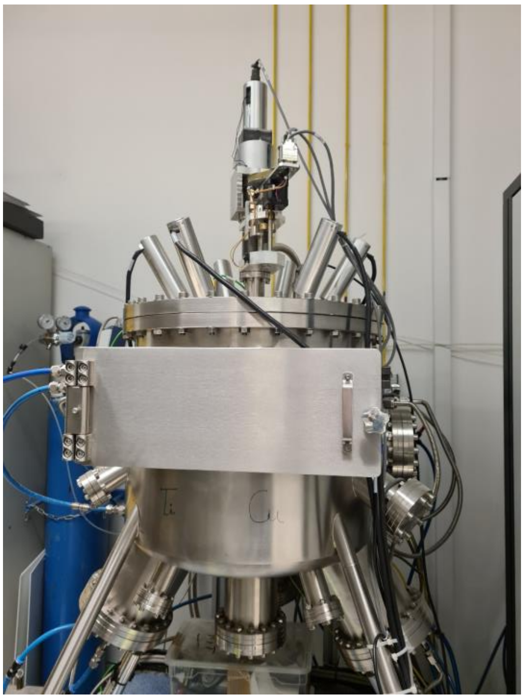

Figure 21. Sputtering equipment at UPTEC.

4 Results and discussion

The present work aimed to characterize the electrical behaviour of selected thermoplastic composite materials to replace metals commonly used to build electronic housings. Characterization includes electrical resistivity measurement through-plane and in-plane and electromagnetic interference shielding effectiveness measurement. Low electrical resistivity is needed for good grounding in the enclosure, and for that, laser ablation and metallic coatings were also investigated in order to improve contact and reduce resistivity between parts. The first stage of this project was to identify commercially available thermoplastic materials that could be characterized and applied in electronic enclosures. This search has focused on low-density materials, the type of matrix and filler of the composite, and the electrical properties since they need to be electrically conductive. The selected materials are described in Table 2, where it can be found matrixes like PBT, PC, PA6 and PA66. The chosen fillers range from carbon fibres, nickel-coated carbon fibres, graphite, carbon black, and steel fibres.

4.1 Shielding effectiveness of commercial materials

EMC is achieved through the shielding of electromagnetic interference, which is essential for electronic housings in the automotive industry. The material absorbs or reflects the incident signal and this measurement was performed for a range of frequencies from 10 MHz to 6 GHz. Shielding effectiveness of commercial thermoplastic composites was measured for seven different materials (A-G). These results were calculated with Equation (3) and are shown in Figure 22.

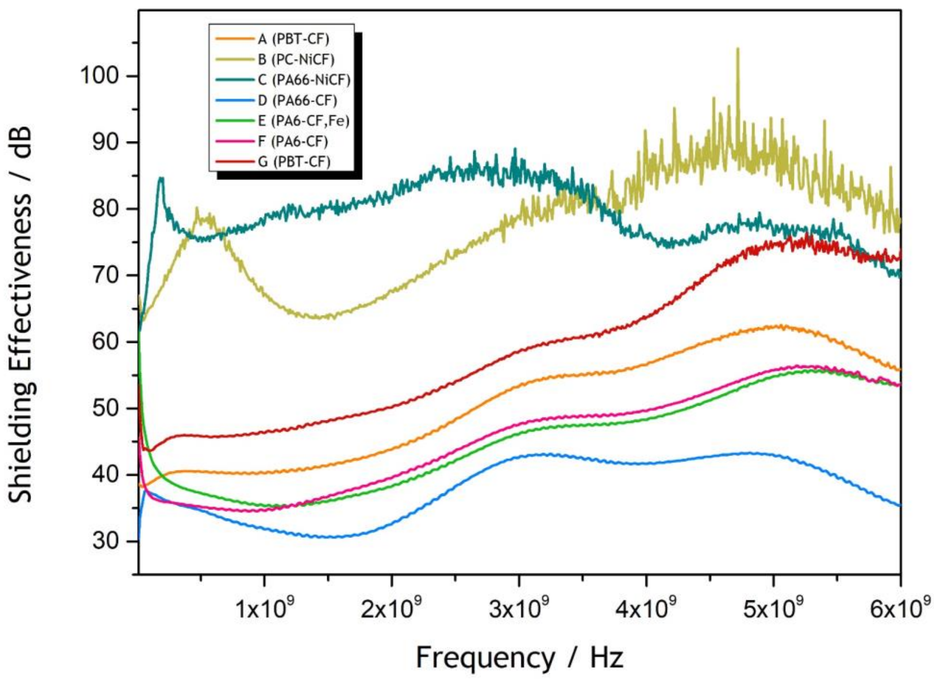

Figure 22. Shielding effectiveness for commercial injected thermoplastic composites (A-G).

The two best performing materials over the entire range of frequencies are Material B and C. These materials fillers are nickel-coated carbon-fibres, which might increase the reflection mechanism from metallic presence that is characteristic for metals. For frequencies below 3 GHz, Materials D, E, and F are under 40 dB, which is not adequate for electronic applications in automotive industry however can be applicable in situations with lower requirements. The common denominator for these three materials is the PA matrix (PA6 for Material E and F and PA66 for Material D). Material A and G with PBT matrixes perform adequately for the desired application being above 40 dB for the whole range of frequencies, but it does not achieve the levels of Materials B and C. The applicability of these materials also depends on their electrical resistivity since for electromagnetic compatibility there needs to be good grounding which requires conduction of electricity across the entire enclosure. Another aspect that determines if the material is viable for industrial application is its cost. A compromise between performance and cost must be made to decide if it's feasible for the automotive industry. Even if the material is too expensive to justify its use in automotive, it can still be used for aerospace applications.

4.2 Electrical resistivity characterization

The electrical resistivity of the selected commercial injected thermoplastic composites was measured to characterize their electrical behaviour and their ability to perform as according to the requirements. Volumetric and superficial electrical resistivity are both important parameters to ensure excellent grounding in electronic housings.

4.2.1 Volumetric resistivity

The electrical resistivity measured through-plane was determined using the experimental setup presented in Figure 17. The obtained results for all the materials studied (Mat A-G; Table 2) are shown in Figure 23. The volumetric resistivity of Sample B was not possible to determine in this setup. The latter result could be related to the filler distribution and orientation in the matrix as it will be demonstrated forward.

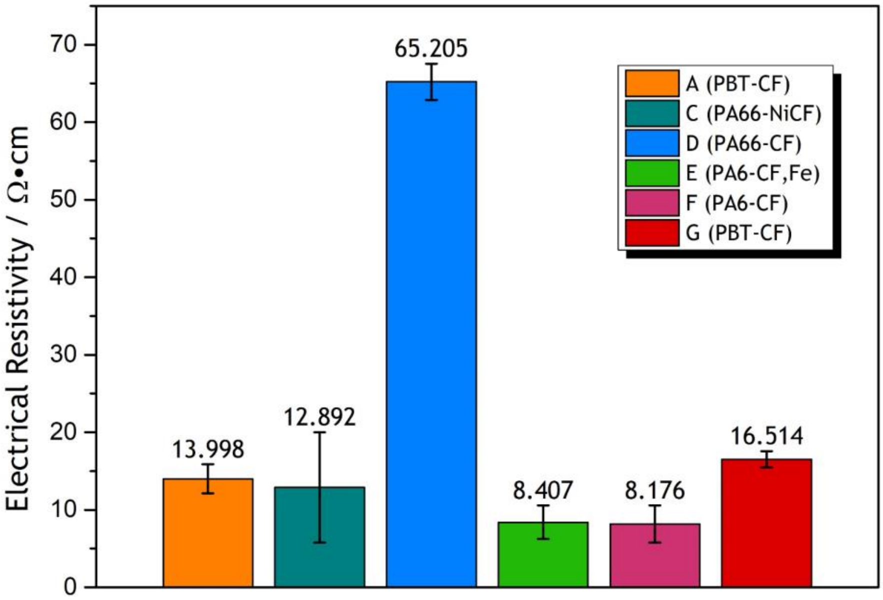

Figure 23. Volumetric resistivity of commercial injected thermoplastic composites.

From Figure 23, it is possible to observe that sample MAT-D, PA66 matrix and ~20% carbon-fibre filler displays higher volumetric resistivity than most of the other materials that vary from ~8 Ω·cm to ~17 Ω·cm. It is possible that the reason for such a result might arise from the type of matrix used since Material A presents almost the same constitution as Material D except for the matrix being PBT instead of PA66.

The volumetric electrical resistivity of Material B was obtained by measuring its impedance on the setup presented in Figure 18. For comparison purposes, Material A and C, with the lowest and highest variation in the first methodology, were also characterized. These materials were also some of the best performing ones in EMI shielding. In Figure 24 it is presented the electrical resistivity through-plane of these materials, in which Material B displays a considerably higher resistivity, ca. 851.51 Ω·cm, than Material A and B, with 56.00 Ω·cm, 28.66 Ω·cm, respectively.

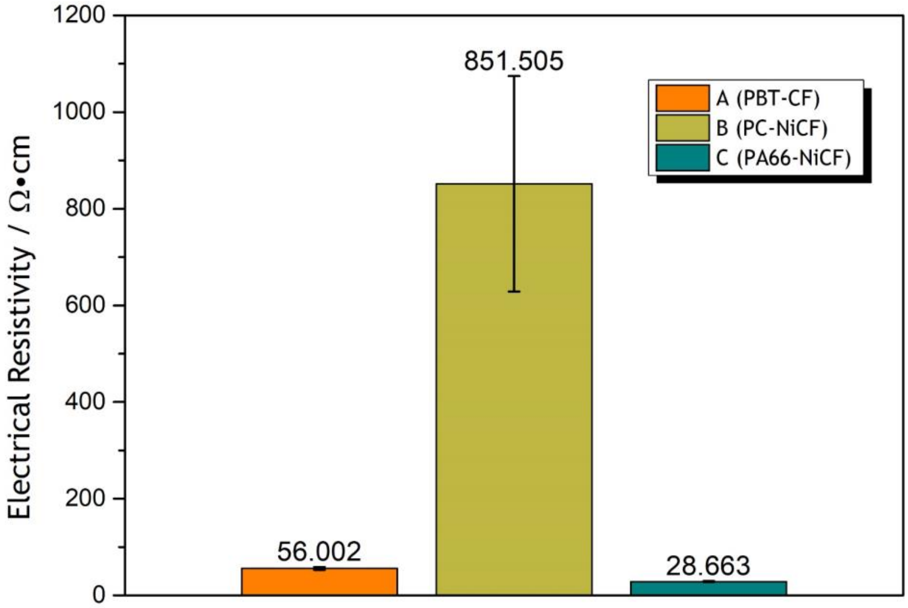

Figure 24. Volumetric resistivity – Impedance method

To explain the lack of conductivity displayed by Material B in the through-plane direction, cross-section analyses by scanning electron microscope (SEM) were performed on the three selected materials. In **Error! Reference source not found.** it is shown the filler orientation and d ispersion through the polymeric matrix of Material B that presented higher volumetric electrical resistivity. Material B has well dispersed and highly oriented fillers, lacking connectivity between fibres in the through-plane direction resulting in anisotropic electrical behaviour, thus high volumetric electrical resistivity. In the cross-section SEM analyses of Materials A and C, Figure 26 left and right respectively, it is observed a better conducting network due to more randomly oriented fibres. The latter explains why a lower volumetric electrical resistivity is observed for these two materials since connectivity of fillers in the through-thickness direction is achieved.

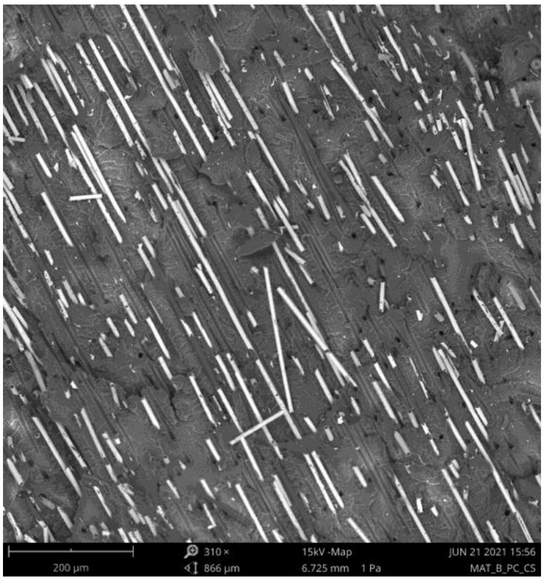

Figure 25. Cross-section of material B

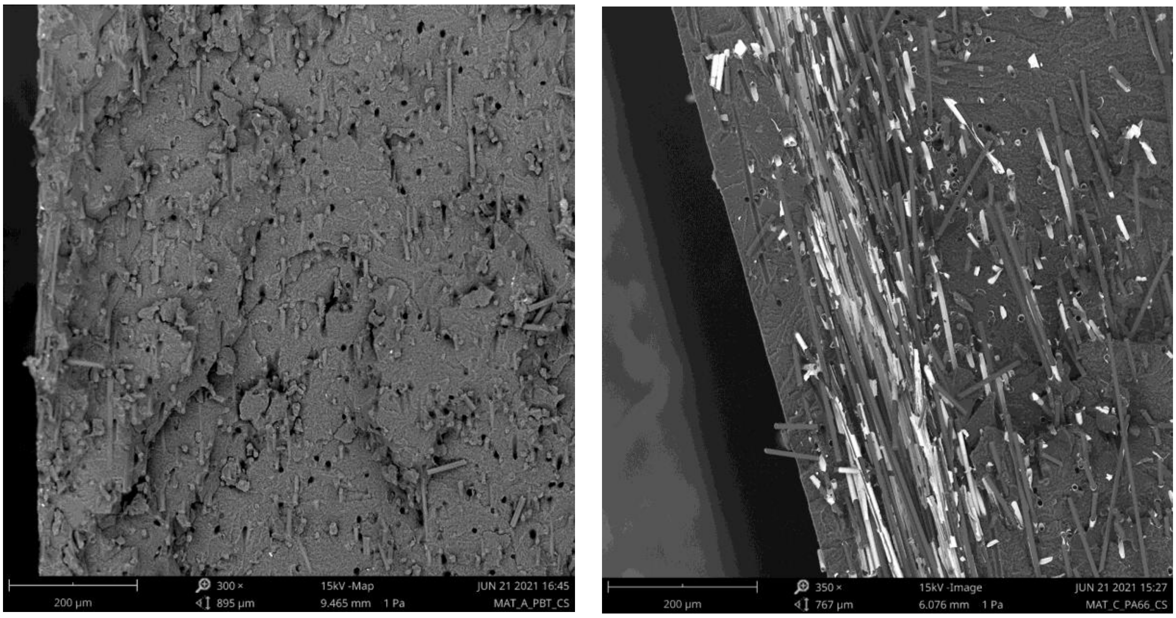

Figure 26. Cross-section of material A (left) and C (right).

4.2.2 Superficial resistivity

The surface resistivity, also called in-plane resistivity, is also an important parameter when selecting a material for building electronic housings for the automotive industry.

Accordingly, the surface electrical resistivity of the selected materials (A-G) was also measured. Here two different measurements are performed according to the injection direction, perpendicular and parallel, due to possible preferable arrangement of the fillers in the injection process. These measurements were performed employing the 4-point method.

The electrical surface resistivity measured parallel to the injection direction for the seven materials (A-G) is presented in Figure 27. In Figure 28 it is shown the obtained results for the perpendicular direction.

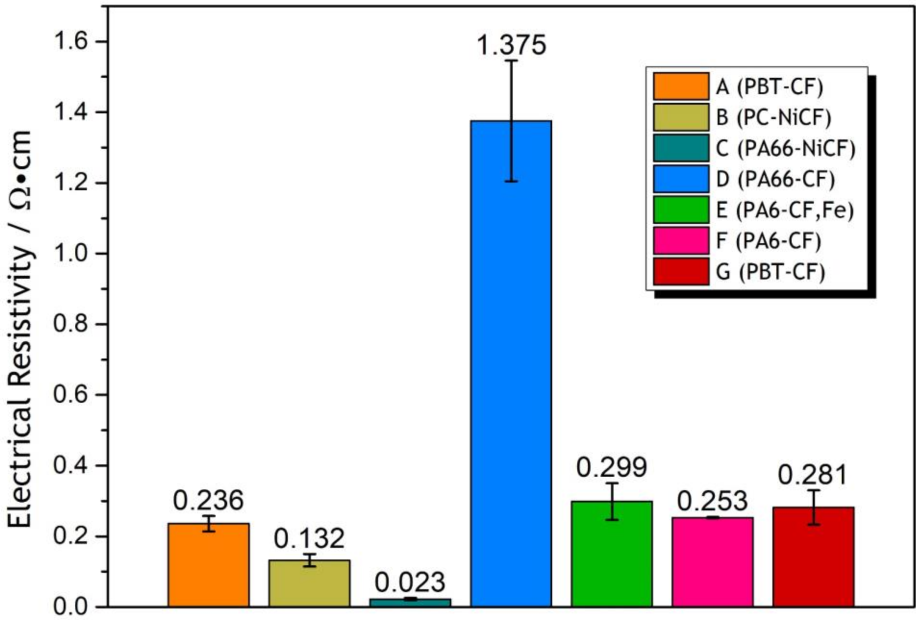

Figure 27. Superficial electrical resistivity parallel to injection direction of commercial injected thermoplastic composites.

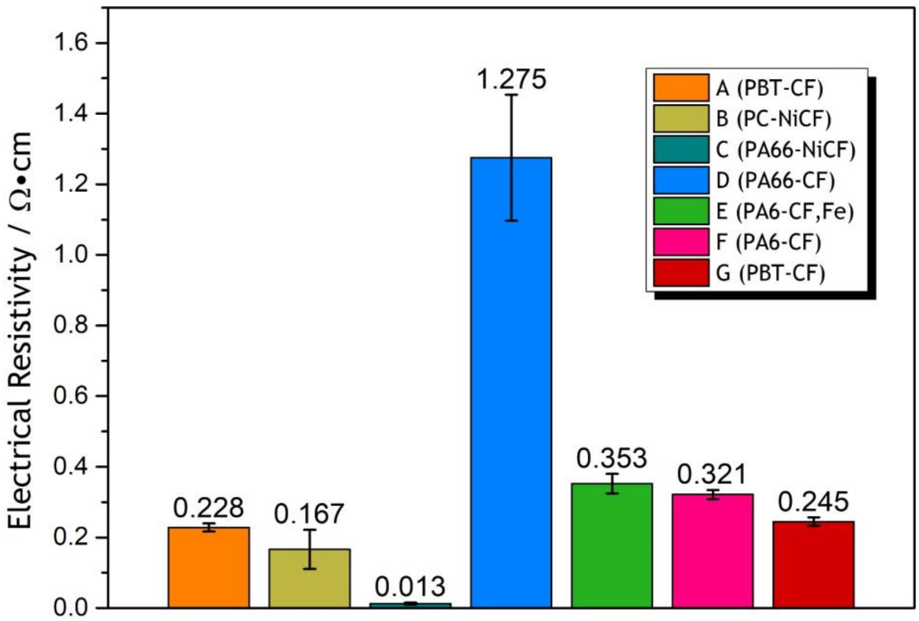

Figure 28. Superficial electrical resistivity perpendicular to injection direction of commercial injected thermoplastic composites.

From the results presented in Figure 27 and Figure 28, most of the materials have a superficial electrical resistivity below 0.4 Ω·cm, except for Material D, which shows the same behaviour as for the volumetric electrical resistivity. On the other hand, Material B now possible to be measured being the second-best material in terms of superficial electrical resistivity, averaging

0.132 Ω·cm for the parallel direction and 0.167 Ω·cm for the perpendicular. The difference between volumetric and superficial resistivity confirms its anisotropic behaviour. Material C was by far the best material, being recorded a superficial electrical resistivity of 0.023 Ω·cm for parallel direction and 0.013 Ω·cm for the perpendicular one; confirming that the nickel-coated carbon-fibres materials were the best-performing ones.

Overall, no significant difference between parallel and perpendicular directions was observed, indicating that there is no preferred alignment in the in-plane direction during the melt processing on the studied materials.

4.2.3 Strategies to improve electrical surface contact/conductivity

To lower the superficial and volumetric resistivity, laser ablation technique was optimized to remove the insulating skin of the polymer typical of the injection process and expose the fibres underneath. A metallic coating was also applied to the laser-ablated surface to further improve the superficial contact of the material. These techniques were performed in materials A, B, and C. The choice of these materials was based on the results of the volumetric and superficial electrical resistivity obtained with the first method and on their performance in the shielding effectiveness tests. Materials B and C are the two best performing ones in terms of superficial electrical resistivity, while Material A is the most consistent. Material B was also chosen to investigate if its volumetric electrical resistivity would be improved by applying these strategies. The volumetric and superficial electrical resistivities were then measured to verify the effect of these post-processing techniques in the electrical properties of the selected materials.

4.2.3.1 Laser Ablation

Several preliminary tests were performed to optimize the operating parameters of the laser. These tests were carried out in spare samples, and the obtained results were confirmed by SEM analysis to infer if the fibres were well exposed and if the material removal was uniform. The best results were obtained for the conditions presented in Table 3, and Figure 29 shows the effect of these parameters on the surface of materials A (top left), B (bottom) and C (top right). These images confirm that no preferred alignment in the in-plane direction occurs as predicted from the superficial electrical resistivity results.

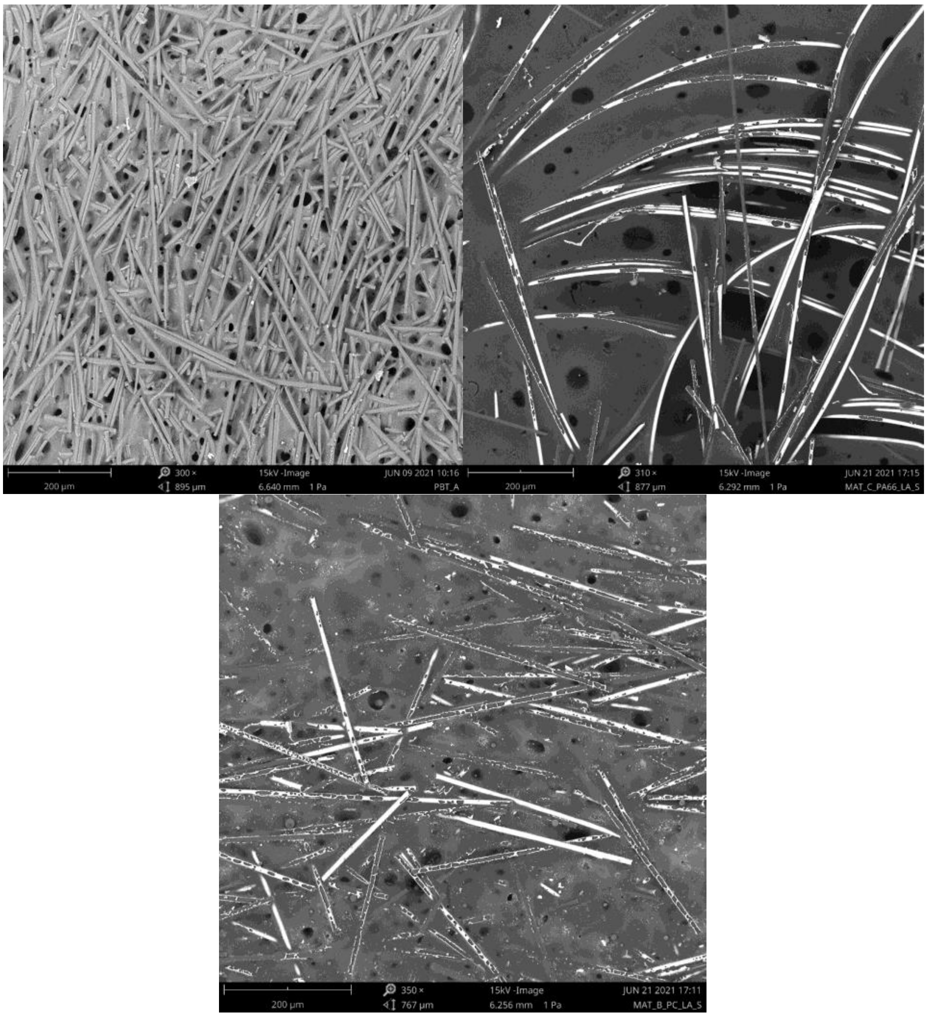

Figure 29. Surface morphology of material A (top left), B (bottom) and C (top right) after laser ablation.

The laser ablation to expose the fibres underneath the skin layer was successful as it can be seen in Figure 29. Although, for Materials B and C one more passage needed to be done with the same conditions as Material A since the removal was not as good. Also, for the 60mm discs of Material C the laser was not removing enough, and the mark speed was reduced resulting in a better removal.

The depth removed by laser ablation was also analysed, being ~21 µm, 8 µm, and 26 µm for materials A, B, and C respectively.

The effect of the fibres exposure was assessed by measuring the electrical resistivity for the laser-ablated materials.

Following, the volumetric electrical resistivity of the laser-ablated materials was measured, and the obtained results are shown in Figure 30. Material A and C present identical electrical resistivity to that of the material before the ablation, while Material B was again impossible to measure. Material A and C results might be due to bad contact with the electrodes or sensitivity issue of the equipment/setup. Another explanation can be a decrease in the contact area due to air between the fibres in the surface which was not accounted for the resistivity calculation.

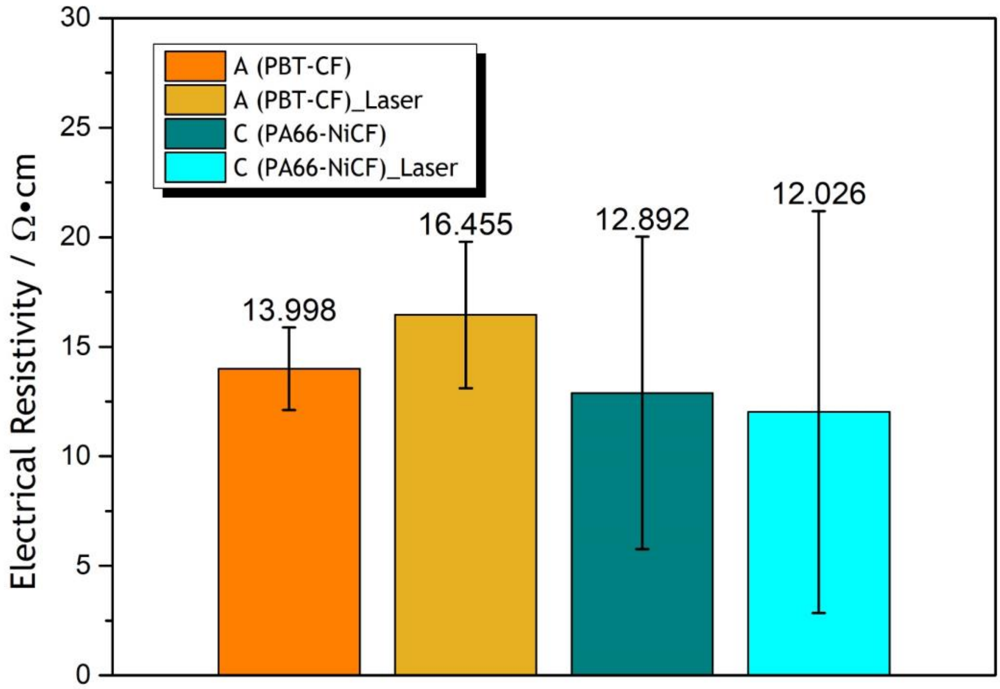

Figure 30. Volumetric electrical resistivity for laser ablated materials A and C.

To evaluate and confirm the results obtained for the laser-ablated materials, the impedance method was again used to measure the volumetric resistivity, being the obtained results presented in Figure 31 for material A and C. These exhibit a significant reduction in resistivity going from 56.002 Ω·cm to 31.498 Ω·cm for Material A and from 28.663 Ω·cm to 1.939 Ω·cm for Material C. For materials A and C there was a clear improvement in their conductivity properties when the insulating skin was removed. Nevertheless, for Material B the behaviour was different for the two samples measured, one reducing the resistivity slightly while the other increased significantly - Figure 32. The difference in results from the two methods is possibly due to the pressure applied in each method being higher in the impedance one. The contact might also be better for the impedance method since the electrodes are copper foils that, with pressure can adjust to the surface of the material.

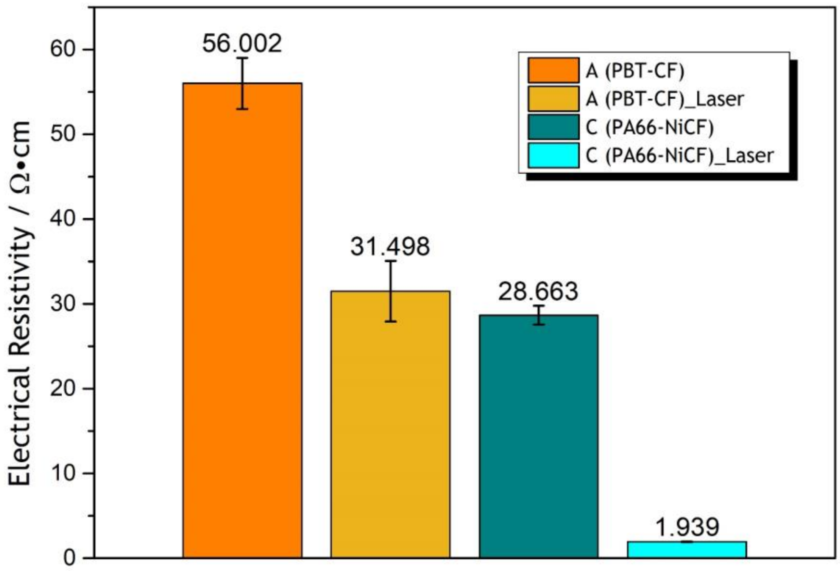

Figure 31. Volumetric electrical resistivity measured through impedance method for laser ablated materials A and C.

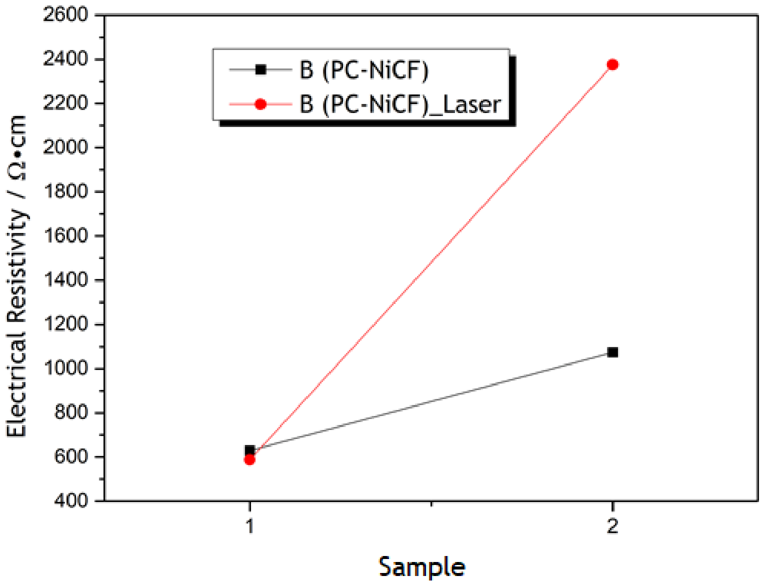

Figure 32. Volumetric electrical resistivity of Material B measured through impedance method.

Superficial electrical resistivity was again measured in both directions to investigate the effect of removing the skin layer.

The superficial resistivities of Material A, B and C, for parallel and perpendicular directions, are presented in Figure 33 and Figure 34, respectively. As it is observed, these results follow the pattern of the volumetric electrical resistivity, i.e. there is not a significant difference between non-treated samples and treated ones, except for Material B. The latter, which laser ablated samples exhibited higher superficial electrical resistivity than those without ablation.

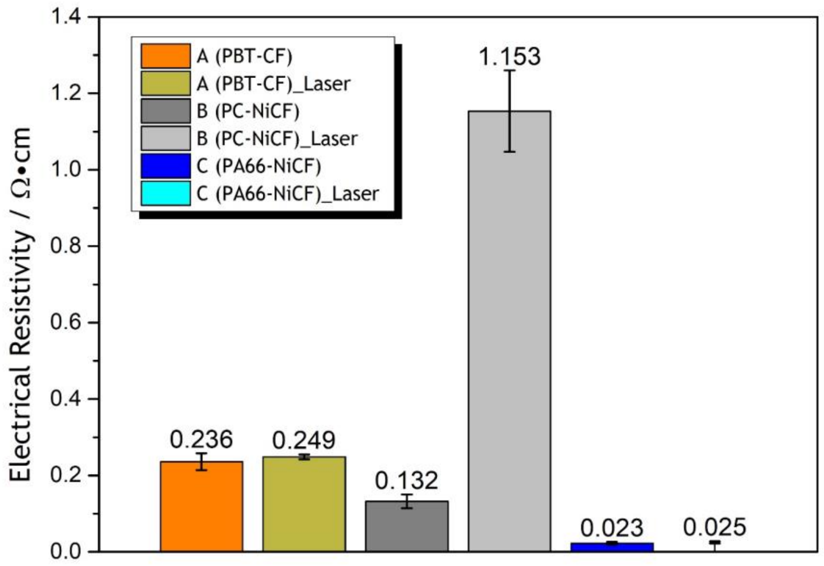

Figure 33. Superficial electrical resistivity for laser ablated materials A, B and C in parallel direction to the injection flow.

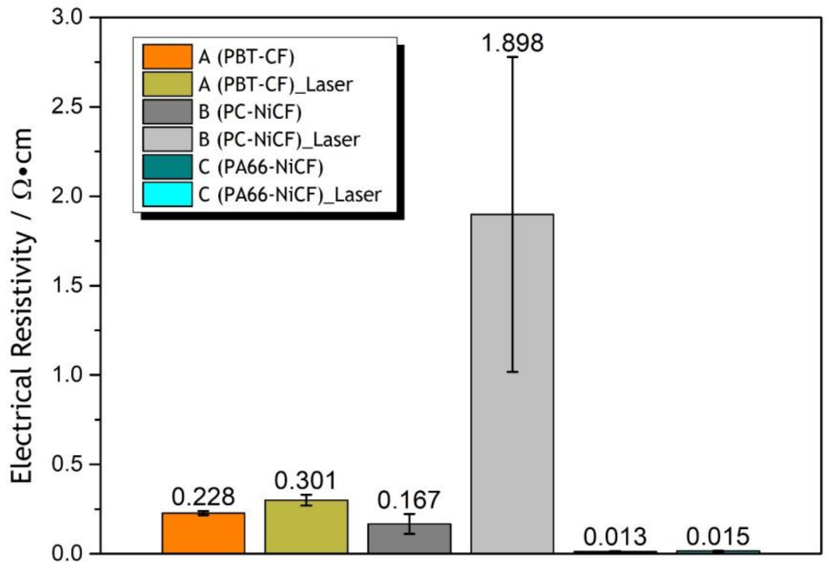

Figure 34. Superficial electrical resistivity for laser ablated materials A, B and C in perpendicular direction to the injection flow.

Overall, it is possible to verify that removing the skin layer of injected thermoplastic composites and consequently exposing the fibres underneath results in a decrease of electrical resistivity. This technology allows for remotion in localized areas for the contact between pieces improving the conductivity.

4.2.3.2 Coatings

Metallic coatings were then applied to the laser ablated samples of Materials A, B and C, in an attempt to further improve the surface contact for the volumetric electrical resistivity.

The sputtering technique was only applied to the volumetric samples. If applied for superficial ones, when measuring the resistivity, it would be obtained an approximate value for the metallic coating and not the material specifically.

The results of this measurement are presented in Figure 35. The volumetric electrical resistivity for metallic coated Material B is presented in Figure 36.

The electrical resistivity increased for materials A and C being more significant for C. For material B there is no comparison to be made through this method since it was impossible to measure it until the coating was applied. After applying a thin copper coating on laser-ablated samples of material B it was possible to measure the volumetric electrical resistivity with the resistivity setup. Nonetheless, as it is observed in Figure 36 a considerable variation was noticed between samples of this material.

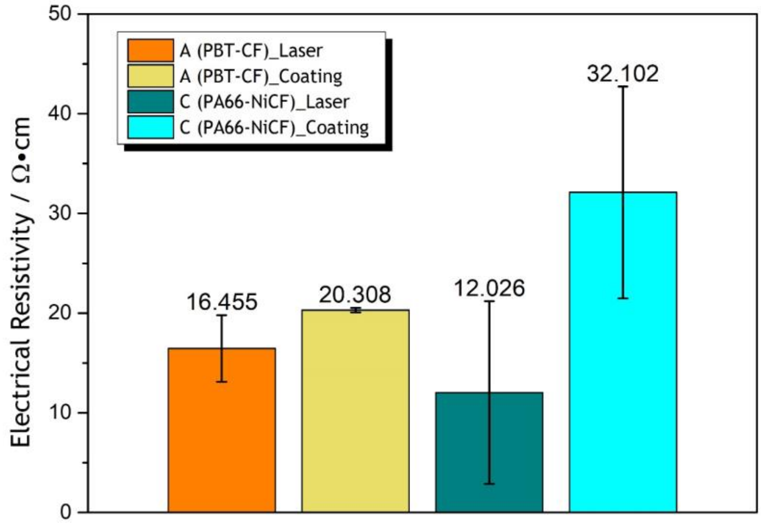

Figure 35. Volumetric electrical resistivity of metallic coated materials A and C.

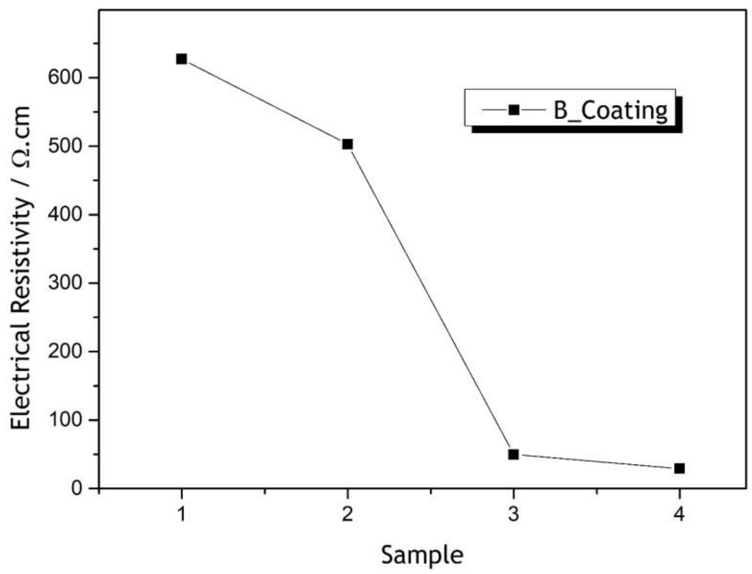

Figure 36. Volumetric electrical resistivity of metallic coated Material B.

Two disc samples of Material A were also coated with the same thickness of copper since within the three materials A, B and C, it was the one with the most reproducibility and the most reliable. These samples were coated for the volumetric electrical resistivity to be measured trough the impedance method. Figure 37 shows the comparison between electrical resistivity of laser ablated samples with and without coating.

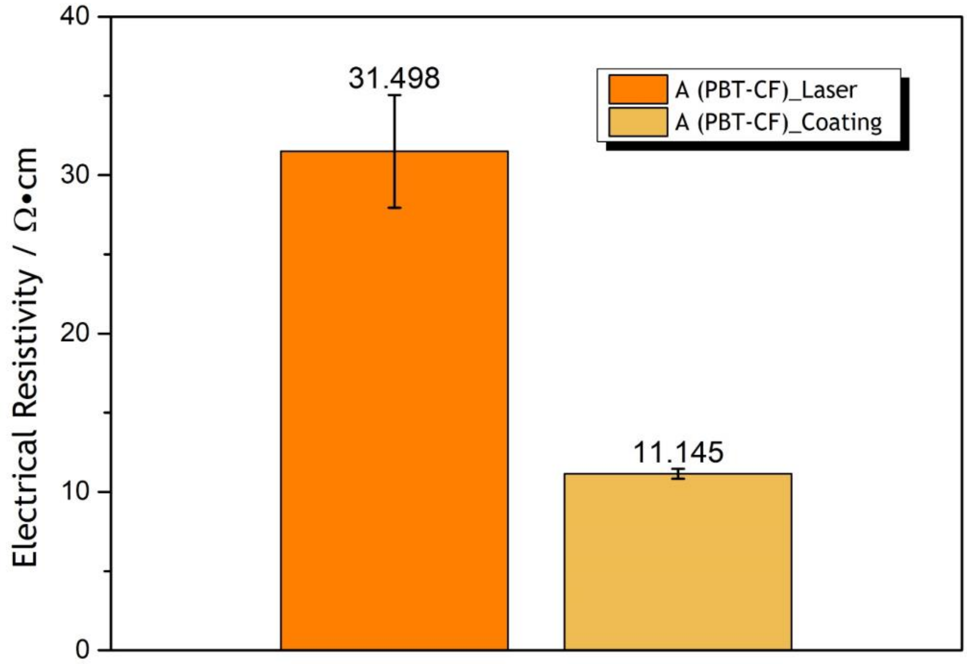

Figure 37. Volumetric electrical resistivity measured through the impedance method for Material A.

The volumetric electrical resistivity decreased significantly, which might indicate that the superficial contact of the material with the electrodes was improved which might be applicable for contacts between adjacent parts of an electronic housing or contacts of PCBs with the enclosure.

Metallic coatings are an efficient way to improve electrical contact between parts, although as a post-processing technique it involves extra expenses. Other coating methods can also produce good results as well as other metals for deposition like aluminium or nickel.

5 Conclusion

With the aim of lowering the weight of vehicles, lower density materials like injected thermoplastic composites were studied to replace metals in electronic enclosures.

In this regard, the electromagnetic interference (EMI) shielding effectiveness (SE) and the electrical properties of 7 commercial materials were studied, (A-G). The selected ones vary on their matrix and fillers.

This dissertation aimed at contributing to the characterization of electrical behaviour, namely volumetric and superficial electrical resistivity, and electromagnetic interference shielding effectiveness of a selected group of commercial injected thermoplastic composites. Also, the improvement of superficial electrical conductivity and electrical contact were also studied.

Material C was the best performing material, making the nickel-coated carbon-fibres an excellent filler for electronic applications. This material had the lowest density making it an excellent replacement of metals. An also strong combination was the PBT matrix with carbon-fibre being one of the most promising ones.

Post-processing treatments were also applied, such as laser ablation and metallic coatings to the most promising materials, based on EMI SE results, to further improve the electrical properties.

Laser ablation treatment was an excellent technique to expose the fibres and improve the overall electrical conductivity of the material. This technique is also easily industrialized.

Metallic coatings application resulted in a better electrical contact reducing the volumetric electrical resistivity. Nonetheless, the interface created between polymer/fillers and the material must be studied further to better understand if any additional resistance is being introduced into the system. Additionally, metallic coatings can be a viable option to improve the contact between parts of an enclosure or even between the enclosure and the printed circuit boards inside.

Despite the improvement, these techniques bring additional cost to the overall manufacturing process; thus, it must be examined if the performance enhancement can justify the extra expenses to be applied industrially.

This study showed that injected thermoplastic composites have good performances in electromagnetic interference shielding and, when conjugated with enough electrical conductivity through-plane and in-plane, are good candidates to replace metals in electronic housings resulting in a weight reduction due to lower density of said composites and providing manufacturers with every advantage of using plastics.

6 Assessment of the work done

6.1 Objectives Achieved

The proposed objectives for this dissertation were to characterize the electromagnetic and electrical properties of commercial injected thermoplastic composites and analyse their capability to replace metals in electronic enclosures as well as to study strategies to reduce electrical resistivity between contacting parts. These new materials needed to provide efficient shielding of electromagnetic interference with enough electrical conductivity for good grounding.

EMI SE was successfully obtained for all seven materials. For electrical resistivity some results were not as expected and for that two methods were used for this characterization. Although, the impedance method was only applied for the most promising materials. Some future works can pass through improving the electrical resistivity setup for an increase in sensitivity or better contact with the electrodes. Despite some unexpected results mainly for laser ablated materials, the electrical resistivity measurements were successful providing good results for comparison purposes between the assessed materials.

6.2 Final Assessment

This dissertation was without a doubt a good learning experience that pushed me out of my comfort zone where I got to expand my knowledge in electromagnetics. I was also able to get insight on the tests a product undergoes before being introduced in the market that I wasn't fully aware of. Finally, this project provides a good comparison between several commercial injected thermoplastic composites and proves that they achieve some good levels of EMI SE and can be further improved to replace metals in electronic applications.

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