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Recent advances in carbon-based polymer nanocomposites for electromagnetic interference shielding

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Abstract

Carbon-based nanoparticles have recently generated a great attention, as they could create polymer nanocomposites with enhanced transport properties, overcoming some limitations of electrically-conductive polymers for high demanding sectors. Particular importance has been given to the protection of electronic components from electromagnetic radiation emitted by other devices. This review considers the recent advances in carbon-based polymer nanocomposites for electromagnetic interference (EMI) shielding. After a revision of the types of carbon-based nanoparticles and respective polymer nanocomposites and preparation methods, the review considers the theoretical models for predicting the EMI shielding, divided in those based on electrical conductivity, models based on the EMI shielding efficiency, on the so-called parallel resistor-capacitor model and those based on multiscale hybrids. Recent advances in the EMI shielding of carbon-based polymer nanocomposites are presented and related to structure and processing, focusing on the effects of nanoparticle's aspect ratio and possible functionalization, dispersion and alignment during processing, as well as the use of nanohybrids and 3D reinforcements. Examples of these effects are presented for nanocomposites with carbon nanotubes/nanofibres and graphene-based materials. A final section is dedicated to cellular nanocomposites, focusing on how the resulting morphology and cellular structures may generate lightweight multifunctional nanocomposites with enhanced absorption-based EMI shielding properties.

Keywords

EMI shielding; nanocomposites; graphene; carbon nanotubes; nanocomposite foams

Introduction

EMI shielding consists in the protection of a given component from electromagnetic waves by using enclosures that are made of electrically-conductive or magnetic materials. Due to the ever increasing demand and use of electronic devices that rely on electromagnetic signals and hence the need to avoid possible interferences from other devices, EMI protective elements have been increasingly used for isolating electrical and electronic devices, many types of cables, guaranteeing radio frequency shielding protection against possible interferences in medical and laboratory equipment, among many other applications.

As electrical conductivity is a requirement for attaining proper EMI protection, common EMI shielding materials are based on metal sheets, screens or foams made of steel, copper, nickel or aluminium alloys, owing to their combination of high electrical conductivity and dielectric constant. However, metal-based protective systems display important drawbacks that limit their applications: high density, poor resistance to corrosion, cost processing and an EMI shielding mechanism based on reflection, preventing their use in applications where EMI absorption is dominant, such as in stealth technology, or affecting the functionality and even cause damage to other electronic circuits or components.

Although some of these drawbacks could be solved by the use of conductive polymers, these commonly display some limitations such as low stability during processing, high cost, low thermal stability and as consequence limited service temperature or globally poor mechanical performance. That is why polymer composites containing conductive carbon-based nanoparticles have been recently considered as possible alternative, as they combine in one single material the advantages of polymers with those given by the addition of carbon-based nanoparticles, mainly electrical conductivity while keeping a good balance of mechanical performance and thermal stability (see Figure 1). Likewise, under specific (micro)structural conditions, it has been shown that composites based on polymers with carbon nanoparticles may display a change in the main shielding mechanism against electromagnetic radiation from the typical reflection mechanism observed in metals to a pure absorption or multiple reflection mechanism, allowing to extend their applicability and enabling their consideration as materials for advanced EMI shielding applications, as in the already mentioned stealth technology. Such is the particular case of foams prepared from said polymer nanocomposites, more specifically dealt in the final part of this review.

Figure 1

It has to be noted that the increasing interest in the last years for carbon-based polymer nanocomposites as elements for EMI shielding applications has been possible first of all by the advent of carbon-based nanoparticles, more specifically carbon nanotubes, CNTs (single and multiwall carbon nanotubes, respectively SWNts and MWNTs) and more recently graphene-based nanoparticles (monolayer/bilayer graphene, graphene nanoplatelets (GnP), graphene oxide (GO), reduced graphene oxide (rGO), etc.), and especially by the great developments that have been made in the synthesis processes of these carbon-based nanoparticles, mainly in terms of production, a crucial requirement for industrialization, but also in terms of controlling the characteristics of the synthesized nanoparticles (crystalline characteristics, geometry and aspect ratio, possible surface modification and functionalization), and developments in the processes for incorporating carbon-based nanoparticles into polymers.

As metal-based materials are already in use and pretty much fulfil EMI protective requirements, why the hype for carbon-based polymer nanocomposites in EMI shielding? Besides the initially-driven purpose of overcoming the typical limitations of metals (high density, high processing cost, poor corrosion resistance, and so on), carbon-based polymer nanocomposites enable to combine several multifunctional characteristics with the possibility of a tailor-made control of the EMI shielding properties, which will depend, besides electrical conductivity, on characteristics such as shielding mechanism, possible material orientation and hence protective directionality, etc., all of which may be altered during compounding and processing in a much easier way than in the case of metals.

Also, due to their multiphase nature, different scale relations may be considered in polymer nanocomposites, starting with the microstructural characteristics of the matrix (phase(s) morphology, possible crystallization, molecular orientation, …), which may even include the possible generation of a cellular structure in the case of foams, the use of nanoparticles having different aspect ratios and geometries or their combination with other microparticles, etc. Polymer nanocomposites are also more versatile from a processing point of view, enabling an even higher number of microstructural possibilities and hence of final properties. All these considerations, which will be addressed in this review, are extremely important in maximizing the EMI shielding efficiency, explaining the fact that carbon-based polymer nanocomposites are already being used in high technology sectors such as electronics or aerospace.

Nevertheless there is still a high scientific and technological interest in generating more knowledge about these highly complex multiphase materials and further extend their use. The key points to proper understand the scientific aspects are addressed in this review and include the effects of the type of added carbon-based nanoparticles (geometry and aspect ratio); their distribution, dispersion and possible alignment throughout the matrix, and respective difficulties; their functionalization and/or surface modification; the recent consideration on the use of nanohybrids and multiscale hybrids by combining different types of nanoparticles and nano/micro/macro particles, respectively; the optimization of the microstructure of the matrix by means of phase(s) morphology control and/or development of a cellular structure; and last but not least the development of new theoretical models, some of which addressed in this review, that avoid approaches based on trial-and-error.

In terms of current sales figures and market potential of polymer nanocomposites, those containing nanoclay are still the largest product segment, accounting for more than 50% of global market volume in 2014 according to the Global Nanocomposites Market Analysis done by Grand View Research [1]. In terms of volume, carbon-based nanofillers and more specifically CNTs are expected to witness significant growth, with an average annual growth rate higher than 19% until 2022, reaching a market revenue in the USA over 400 million dollars (see Figure 2), boosted by the great interest in the automotive industry for polymer-based materials with enhanced thermal and electrical conductivities, as well as the growing use of nanocomposites in the manufacturing of electrical components and semiconductors for supercapacitors and printed circuit boards.

Figure 2

If CNTs are considered as material (MWNTs and SWNTs, the first being the most used one), its market size was over 2.0 billion dollars in 2017, with annual expected growth rates over 22% until 2024, with clearly polymers representing the most used application (representing about 60% of CNT applications in 2017) [2]. Applications of CNT-polymer nanocomposites in sensors and actuators have been growing in recent years, with epoxy-CNT nanocomposites finding significant applications in the automotive sector, aerospace, fuel cells, turbine blades, EMI shielding elements and radar-absorbing materials. Owing to their extremely high electrical conductivity, the addition of CNTs to polymers is expected to lead to novel electrically-conductive polymers, thus expected to represent the most important application of CNTs among polymer nanocomposites in terms of consumption (see Figure 3). However, expected market growth rate may be hindered in part by the high costs associated to the production of a high amount of CNTs with the required quality, as well as possible safety issues related to prolonged exposure to nanoparticles by employees.

Figure 3

Being a newer material, graphene-based materials, namely GnP, GO and rGO, although representing a lower market revenue than CNTs, are expected to reach almost 75 million dollars revenue and over 500 ton by 2022 (Figure 4), according to a recent report by Grand View Research [3], with emerging economies like China or India expected to boost its growth during the next 5 years, for both research and development, as well as its expected use in various industries, including electronics and aerospace [4].

Figure 4

1. Carbon-based polymer nanocomposites for EMI shielding: composition, microstructure and general properties

1.1. Types of carbon-based nanoparticles and general properties

Carbon-based nanoparticles have recently attracted a great deal of attention owing to their inherently high mechanical performance and outstanding transport properties, especially in leading sectors such as electronics. Due to their structure-dependent conductivity, their addition into polymers could solve some transport properties-related issues of composite materials at low or even extremely low concentrations for applications that can go from electrostatic discharge, ESD (fuel system components, packaging materials for ESD sensitive items, etc.) to electrostatic painting, up till EMI shielding (fuel cells, gaskets for electronic devices, among others) [5-8]. Due to their reduced density, the use of polymer-based composite materials with added functionalities resulting from carbon-based particles has received a great deal of interest for light-sensitive components [9-11].

Carbon-based nanoparticles may be classified according to their structure and dimensions. The most common particles are carbon nanotubes (CNT) and more recently graphene, alongside carbon nanofibres (CNF) and nanometric-sized carbon black (CB) (see Figure 5). CNTs, graphene and their derivatives are low density materials in the nano scale, making them suitable candidates to be used in the fabrication of high performance polymer composites. Their geometric characteristics provide the possibility of high surface interaction with polymers, which could result in significant mechanical and/or transport properties enhancements.

Iijima’s study [12] on fullerenes in 1991 led to the discovery of CNTs, which have attracted a great deal of scientific attention ever since due to their potential in various applications, despite remaining issues such as availability and high cost of high quality CNTs, limiting their use in the development of CNT-reinforced polymer nanocomposites at industrial scale [13]. Individual CNTs can be seen as hollow cylinders of a hexagonal network of single layer carbon atoms with the end capped with half of a fullerene having a diameter between 1 and 50 nm [14]. Regarding the number of graphitic layers forming the structure, CNTs are usually categorized in single and multi-wall nanotubes (SWNT and MWNT, respectively). SWNTs are cylinders formed by one single curved carbon layer with a typical diameter between 1 and 2 nm, whereas MWNTs consist of multiple concentric cylinders with weak secondary van der Waals bonds maintaining them together with a Russian-doll like structure [15-17]. The diameter of MWNTs can vary depending on the number of layers, with typical outer diameter in the order of 10-50 nm [5]. Depending on the orientation of the graphite lattice relative to the axis of the cylinder, which defines the chirality or helicity of the nanotube, CNTs may display variable structures: armchair, zig-zag or the so-called chiral structure. CNTs having an armchair structure display a metal-like behaviour (conductive), zig-zag CNTs behave as semiconductors, and those having a chiral structure act as diodes.

Figure 5

Electrical conductivity enhancement by several orders of magnitude at very low carbon nanoparticles concentration benefits the production of nanocomposite material for EMI shielding applications [18-20]. The electrical properties of nanocomposites reinforced with CNTs depend on nanotubes' diameter, number of concentric carbon layers and chirality, providing convenient tuning control for both electrical and magnetic response [21].

The 2010 Noble prize in Physics, awarded to Andre Geim and Konstantin Novoselov "for noble experiments regarding the two-dimensional material graphene", was the beginning of endless scientific research opportunities. Among carbon-based nanoparticles, graphene has caught a large amount of attention due to its extraordinary combination of properties, such as high surface area, aspect ratio, tensile strength, electrical and thermal (5000 W/(m·K)) conductivities [22-24], high EMI shielding efficiency, flexibility, transparency or low coefficient of thermal expansion [25-29]. Graphene, being a carbon allotrope, is formed by a honeycomb-like carbon lattice with hexagonal oriented carbon atoms in a 2D layer, forming graphite when stacked together [30]. Graphene could be a suitable substitute for CNT in terms of feasibility and cost due to its excellent in-plane properties [31]. However, the struggle for obtaining complete and homogenous dispersion of individual graphene layers in a solvent remains unsolved [32], challenging the synthesis and processing of bulk-quantity graphene sheets.

On the other hand, CNFs have received special attention owing to their large axial ratio, besides good mechanical and transport performances. However, CNFs present a smaller surface area, which could have a negative impact on some applications such as catalysis. Nonetheless, previous studies demonstrate that their axial ratio favors the catalytic performance, specifically in terms of electrons' transfer-based processes such as photocatalysis [33-37]. Other applications of CNFs include lithium ion batteries [37], solar cells [38], supercapacitors [39] and fuel cells [40-41], among others. The diameter of CNFs varies between that of CNTs and carbon fibres (around few hundred nanometers). A major difference of CNFs when compared to CNTs is their graphene layer orientation, as they show lower regularity. Besides that, CNFs also present graphitic edge terminations on their surface, i.e., a higher level of imperfection, in comparison with CNTs [5].

Carbon black (CB) is a filler commonly used for modifying the mechanical, electrical and optical properties of polymers [42]. Besides its massive usage in automotive industry at high concentrations, it has been investigated as a nanofiller for improving electrical conductivity [43-45]. Commonly available CB particle diameter varies from

10 to 50 nanometers with a morphology composed of aggregates of spherical primary particles with turbostratic disordered layering [46].

1.2. Surface modification/functionalization of carbon-based nanoparticles

As previously mentioned, a fine dispersion of the nanoparticles in the matrix, commonly achieved by prolonging the duration of mixing during melt-compounding, facilitates the enhancement of the mechanical and electrical properties of the final nanocomposite. However, this can dramatically reduce the aspect ratio of the nanoparticles due to partial rupture during processing or degradation. Other methods such as in-situ polymerization and ultrasonication have proved effective in achieving homogeneous dispersion [47]. Another method for enhancing the dispersion level considers the prior modification and functionalization of the nanoparticles, which is a possible strategy for enhancing the electrical conductivity of carbon-based reinforced nanocomposites at lower nanofiller concentration [48-49].

In the case of CNTs the improvement of the specific properties of the nanocomposites is strongly influenced by the functionalization method and its extension [50]. The modification of the CNTs can be divided in two main groups: firstly, utilizing carboxylic acids [51] and secondly by means of a direct attachment of functional groups to the carbon-carbon surface layer [52]. Concerning the first category, previous works show that the introduction of carboxyl groups to prior oxidized CNTs can be useful due to the possibility of further modifications as they enable the covalent coupling via the creation of amide and ester bonds or other functional moieties for which purpose bifunctional molecules (e.g. diamines) are often utilized as linkers to dendrimers, nucleic acid, enzymes metal complexes, among others [53]. Using a mild oxidation of

CNTs in the presence of nitric acid minimizes the possible shortening of the nanotubes, retaining the electronic and mechanical properties of the functionalized CNTs [54].

In the second category of functionalization, the addition of sidewall reactive groups has been shown to lead to a better improvement of the electrical and mechanical properties [55]. One of the most common thermally-activated chemical functionalizations used with direct attachments consists of the fluorination of nanotubes [56-62] in order to avoid agglomeration of CNTs in the matrix and to increase the surface energy and adhesion properties of the CNTs [55]. The electrochemical modification in the bulk form and single nanotube and photochemical functionalization have also been studied by multiple researchers [63-68].

While graphene inherently possesses high electrical conductivity, some applications require chemical surface modifications such as graphene oxidation, reduction, or other functionalization methods to enhance properties such as stabilization via structural tuning. Chemical modification of graphene can be achieved through both covalent and noncovalent methods [69-71].

Attaching extended functionalities onto graphene's surface using covalent bonds usually happens through oxygen linkages or structural π-π network [69]. Common covalent attachments on pristine graphene consider organic functionalities that can be a free radical attached to sp^2 carbon atoms of graphene [72-76], which can be used to tune its physical and electrical conductivity properties. Alternative organic attachment functionality can be done through covalent modification of graphene using dienophiles [69]. This technique has applications in biotechnology, nanoelectronics, drug delivery and solar cells using azomethine ylide reacting through 1,3-dipolar cycloaddition [77-79] or, as He et al. presented in their work with various graphene functionalizations using nitrene cycloaddition, resulting in improved chemical and thermal stability compared to GO, while retaining its high electrical conductivity, with possibility of further modifications [80].

Covalent modifications are commonly used in graphene derivatives such as GO. GO is a layered material consisting of hydrophilic oxygenated graphene sheets carrying oxygen functional groups [81] of hydroxyl, epoxy, carbonyl and carboxyl on their basal planes and edges, which allows the attachment of other functional groups through typical organic reactions, such as amidation, silanization, esterification, substitution and cycloaddition [69]. Modification via amidation provides reaction of GO to functional molecules such as amino acids [82], casein phosphopeptides [83], polyethylene glycol (PEG) [84-85], chitosan [86], polyethyleneimine [87-89], acid pectinase [90], poly(L-lysine), polyurethane [91], among others [92-94]. Likewise, amidation, esterification [95-99] and silanization [100-104] are other approaches to modify GO with numerous functionalities [69].

Additionally, due to the mechanisms of graphene synthesis via reduction of GO, the residual epoxy and hydroxyl functional groups [105-107] can be a proper modification for specific applications such as adsorption capacity for CO_2 storage [108]. This method provides a defect-free graphene surface compared to reactions with carbon-carbon double bonds [69].

Non-covalent modification of graphene has attracted attention due to the fact that it does not affect the inherent properties of the 2D sp^2 carbon network [109-110]. These modifications can be done by polynuclear aromatic rings [111-115], surfactant [116-120] and ionic liquids [119-122], biomolecules and macromolecules [123-129] or attachment of nanoparticles such as silver nanoparticles (AgNP) [130-132], Fe_3O_4

nanoparticles [133-134], gold nanoparticles [135-136] and palladium nanoparticles [137] to graphene's surface.

In order to induce a homogenous dispersion with strong interfacial interaction between CB and the matrix, various surface modifications have been investigated [138]: thermal [139], wet chemical or electrochemical oxidation [140-144], plasma treatment [145-148], photochemical [149], ion or cluster bombardment, reaction with organic compounds [150-152], silanization [153] or polymer grafting [139, 154-155]. CB's proper modification techniques are needed depending on the required properties and application.

1.3. Effects of the dispersion of carbon-based nanoparticles in polymer nanocomposites

Various research efforts have been directed towards the preparation of polymers reinforced with carbon-based nanoparticles for various applications. The agglomeration of nanoparticles during processing and inefficient interaction with polymer remains the main issues for reaching the outstanding properties expected for these multifunctional fillers. In order to overcome these obstacles, sufficient shear forces are required to disperse the nanoparticles and homogenize their concentration in the host matrix. Common methods to reach this goal include different forms of mechanical dispersion such as ultrasonication, calendaring, ball milling, shear mixing, extrusion, roll milling, etc. Nanoparticles' surface functionalization, already discussed in the previous subsection, has also been used for enhancing polymer-nanoparticle interaction. These dispersion techniques can be used alongside the modification of carbon-based nanoparticles to prepare functional nanocomposites for specific applications such as EMI shielding.

1.3.1. Thermoset-based nanocomposites

In-situ polymerization is one of the major preparation techniques for thermoset-based nanocomposites, as in presence of a given nanofiller good bonding can be achieved between the nanoparticles and the matrix. In this method carbon-based nanofillers are mixed with the monomer, polymerization taking place with addition of a curing agent [156]. In this method, utilization of sonication or microwave can provide improved exfoliation of the nanofiller (graphene, CNT, etc.) in liquid pre-polymer state where re-agglomeration would be avoided following the termination of the process by curing. Sharmila et al. [157] showed that microwave-exfoliated rGO in epoxy resin could be a suitable candidate for EMI applications. A study by Yuki et al. [158] presented the preparation of GO/polyurethane (PU)/epoxy nanocomposite with prior sonication of GO in dimethylformamide (DMF) solvent, with the final nanocomposite showing improvements in mechanical and thermal properties. Another study by Battisti et al. [159] demonstrated the enhancement in electrical conductivity of CNTs in liquid state polyester resin using various sonication powers. Mentioned research indicated that the sonication at 100 W caused eventual damage to the nanotubes. The sonication can also be applied in a solution containing both thermoset polymer and the filler in a common solvent or can be utilized to disperse the filler in a solvent prior to mixing with the dissolved polymer [160-163]. In these methods the solubility of the polymer and low viscosity are the requirements that should be taken into consideration. On the other hand, the sonication time, power and mode (probe or bath sonication) are the key factors in governing the efficiency of sonication [156].

Brown et al. [164] presented the effect of sonication on SWNTs dispersion in D2000 (diamine) and epoxy, showing that the dispersion was not feasible in the absence of sonication. Light microscopy of the material sonicated for 15 and 60 min showed that the large bundles of SWNTs broke up, followed by a rupture of the agglomerates, leading to a greater homogeneity.

Intensive stirring of nanofillers in thermosets such as epoxy is another method of dispersion. However, nanofillers such as MWNTs tend to re-agglomerate following few hours of curing [165]. Still, some studies managed the preparation of CNT/epoxy nanocomposites with a conductive network using this method with percolation thresholds as low as 0.0025-0.0050 wt% [166-167]. Similar studies claim that the intensive shear forces employed during stirring are sufficient for achieving a good dispersion level of nanofillers in epoxy resins to form a conductive network at low percolation thresholds [167-169]. Shear mixing using twin-screw mixer has also been used for preparing thermosets prior to addition of the curing agent. As an example, Moniruzzaman et al. [170] showed that a high shear mixing of SWNT/epoxy provided improved dispersion of already sonicated SWNT/resin solution.

Calendaring is another process to obtain a pre-cured mixture of thermosets and carbon-based nanofillers [171], the most common one being three roll milling, which employs a shear force induced by rollers to mix, disperse and homogenize viscous materials [156]. Chatterjee et al. [172] illustrated the preparation of epoxy with expanded graphite using a combination of calendaring with ultrasonication, where the sonicated/calendared samples presented higher mechanical properties. Another study by Gojny et al. [173]

presented good results in achieving well-dispersed CNT and CB in epoxy composites while enhancing the stiffness and fracture toughness of the nanocomposites at low nanotube contents using this technique.

Ball milling is another method that provides improvements in dispersion of carbon-based nanofillers. Intensive pressure is locally generated using the collision of small, rigid balls in a concealed container, which can be used for various purposes [156], e.g. transformation of CNT to nanoparticles [174], generating highly curved or closed-shell carbon nanostructures [175], enhancement of lithium saturation in SWNTs [176], modification of cup-stacked CNTs [177], and generation of various carbon nanoparticles from graphite [178]. A work by Xia and Song [179] demonstrated improvements in mechanical properties of grafted SWNTs on PU with polycaprolactone (SWCNT-g-PU/PCL) using ball milling as dispersion rout. Another study by Sui et al. [180] showed that acid-treated CNT dispersed by ball milling in natural rubber significantly enhanced the mechanical properties of the resulting nanocomposites. In addition, due to radiation absorption of carbon-based fillers, these carbon-based nanoparticles can also be used to cure thermosets by elevating the temperature by means of microwave absorption [181-183].

1.3.2. Thermoplastic-based nanocomposites

As for thermosets, thermoplastics also take advantage of preparation techniques such as in-situ polymerization and solution mixing. The solution containing the polymer and the reinforcement particles can be prepared in a proper solvent using mechanical mixing, magnetic agitation or sonication [26, 156]. Sonication can be applied either to the solution of filler/solvent prior to addition into the polymer [184] or to a solution already containing the polymer. Unfortunately, the dispersion of nanoparticles in host polymers using sonication can damage their structure, due to the long sonication times usually required to break the van der Waals' interactions between nanoparticles, which might not be desirable for some applications. In-situ polymerization can be beneficial to this matter, highly depending on the used polymer [185-186].

In terms of enhancing the electrical conductivity of functionalized nanocomposites, methods such as the latex technology and dry-mixing are promising techniques for preparing highly conductive materials (10^{-2} to 10 S/cm) for EMI shielding purposes [156] (see Figure 6). Latex fabrication method consists of dispersing the filler in an aqueous medium followed by the addition of colloidal dispersion of polymer particles [187]. Besides high electrical conductivity at low percolation threshold, other two main advantages of this method are simple mixing process and the use of water as solvent [188-190]. Dry-mixing is, to some extent, very similar to the latex technology, as the dispersion process consists of mixing the filler with a micro-sized polymer powder, providing a covered polymer granule surface by the filler followed by sinterization [191]. Electrical conductivity measurements done on nanocomposites prepared using these two methods have shown that it is possible to reach higher values than that of randomly dispersed fillers [188, 192].

Figure 6

Contrarily to thermosets, thermoplastics have fewer limits in processing for the preparation of nanocomposites and dispersion of nanofillers in the matrix. In addition to ball milling, ultrasonication, stirring and calendaring, carbon-based nanoparticles can take advantage in thermoplastic nanocomposite preparations via melt-blending, both using continuous processes such as extrusion or batch mixing methods [193], which provide the advantage of avoiding any solvent employment to disperse the filler. Although these methods do not facilitate the homogeneity of filler content in the matrix, requiring the application of intense shear forces and higher temperatures, they are yet the most promising techniques to prepare nanocomposites containing nanofillers at industrial scale for thermoplastics such as polycarbonate (PC) [194], poly(lactic acid) (PLA) [195], polyamide (PA) [196], polyethylene (PE) [197], poly(ethylene terephthalate) (PET) [198], polypropylene (PP) [199], polystyrene (PS) [200], etc. In order to reach a higher level of dispersion and exfoliation, sonication can be applied to break the agglomerated particles prior to their addition into polymers and melt-mixing [201].

Hornbostel et al. [202] represented the different dispersion of SWNTs in PC using melt-mixing and sonication vs. coagulation of PC/CNT in DMF solvent. The micrographs presented in Figure 7 show that a homogeneously fine-doted composite structure was seen in the melt-extruded material, while in the coagulated material a rather flake-like distribution of nanofillers was observed.

Figure 7

As a matter of fact, continuous extrusion has been vastly considered as melt-mixing method to prepare carbon-based polymer nanocomposites. For instance, polymer nanocomposites reinforced with CNTs have been prepared using twin-screw extrusion [203-204], with authors demonstrating the very good distribution and dispersion of

CNTs in the polymer matrix after melt-compounding. A vast selection of publications that consider the preparation of carbon-based polymer nanocomposites by means of continuous melt-mixing extrusion process are included in this review, especially when dealing with the effect of nanoparticle dispersion by means of processing on the electrical conductivity and hence EMI shielding behaviour of polymer nanocomposites.

In a recent review, Spitalsky et al. [205] considered the chemistry, processing, mechanical and electrical properties of CNT-polymer nanocomposites, dedicating a great deal of attention to nanocomposites processing and among processing methods to melt-blending, always with the idea in mind that the effective use of carbon nanofillers such as CNTs in composite applications strongly depends on their homogeneous and individual dispersion throughout the matrix. Among batch melt-mixing techniques, Goh et al. [206] used a laboratory mixing molder to melt-blend PMMA and CNTs, afterwards compression-moulding the resulting mixes to films, and demonstrating the viability of batch mixing to properly disperse CNTs. Zhang and co-workers [207] prepared PA6-CNT nanocomposites containing a fix amount of 1 wt% CNT using a Brabender Plasticorder internal mixer, showing homogeneous dispersion of the nanotubes through PA’s matrix, leading to nanocomposites with enhanced mechanical performance. Bocchini et al. [208] used the same type of internal mixer to prepare LLDPE-CNT nanocomposites, in this case relating the enhanced dispersion of the nanotubes due to the effective shear stresses applied inside the chamber of the internal mixer with a final delay in the thermal and oxidative degradation of the nanocomposites when compared to virgin LLDPE. High performance polymers have also been melt-mixed with carbon-based nanofillers using batch mixing techniques. Such is the case of the work of Kumar and co-workers [209], which used a Sigma high temperature internal mixer equipped with two counter-rotating rotors to melt-mix at high temperature PEI with untreated and acid-treated CNFs. The authors demonstrated that the combination of proper shearing applied inside the internal mixer and acid-treatment of the nanofibres prior to mixing led to improved nanofibre dispersion throughout PEI's matrix and, as a consequence, to enhanced nanocomposite tensile strength and electrical conductivity, especially when using lower CNF loadings (up to a maximum of 1 phr CNF).

In terms of the influence of flow conditions on nanocomposite's morphology, Martins et al. [210] used different strategies to prepare nanocomposites of PVDF-PAni with variable concentrations of nanotubes (0.25 to 2 wt%) using a batch mixer of the Brabender type, i.e., a torque rheometer equipped with a mixing chamber, directly adding the nanotubes into the polymer blend inside the mixer; dispersing the nanotubes in the reaction medium during PAni polymerization, blending it afterwards with PVDF in the mixer; or using a combination of both methods. Depending on the used strategy CNTs were mainly located in PVDF's phase, in PAni's phase or in both phases, leading to the formation of a percolated CNT network at a minimum of 1 wt% CNT in the first case, no percolation in the second and percolated network at 2 wt% CNT in the last case. Recently, Vilaverde and co-authors [211] analyzed the influence of flow conditions on the dispersion and re-agglomeration of GnP in PP. For that purpose, they used a prototype small scale modular extensional mixer, which enabled to apply a sequential first mixing step, followed by melt relaxation and a second mixing step, which authors used to reproduce the flow conditions of the first step or generate milder flow conditions. While the gradual decrease in size and number of GnP agglomerates at 2 and 10 wt% GnP concentrations at the end of the first stage was done at a rate that was independent of the applied flow conditions, the application of a second mixing stage to a re-agglomerated GnP morphology material obtained at the end of the relaxation step led to variable GnP dispersion results that were highly dependent on the applied stress flow conditions.

As flow conditions strongly affect the final morphology of the resulting nanocomposites and ultimately their final performance, a good number of research groups have dedicated their investigation to the development of mixers with enhanced mixing capability. In this sense, Sundararaj's research group has developed a miniature mixer with enhanced shear mixing and complex elongational flow modes required for optimum dispersive mixing, which they called the "Alberta Polymer Asymmetric Minimixer" (APAM), specifically thought for mixing multiphase polymer systems and composites [212-213], demonstrating that the final morphology of polymer blends was similar than that obtained in internal mixers or in twin-screw extruders, with the advantage of requiring much lower material amounts [212]. Comparatively, both experimentally [212] as well as using flow simulation [213], the authors demonstrated that the APAM mixer allowed a proper dispersion of nanofibres in polymer matrices comparable to the internal batch mixer and much better than other mixers such as the MiniMAX, which relies only on simple shear flow patters, where nanofibres remained aggregated and not fully covered by the matrix. Nevertheless, the high shear stresses applied during mixing led to partial rupture of nanofibres.

As can be seen, researchers that have considered the preparation of carbon-based polymer nanocomposites through melt-mixing have focused their work in counteracting the main limitations of both continuous and batch melt-mixing methods, which are related to the high shear stresses combined with relatively high processing temperatures required to guarantee proper nanofiller dispersion in polymer matrices, especially when compared to solution mixing methods, and the fact that nanofiller addition results in a significant increase in viscosity, limiting processing and making it harder to guarantee a proper nanofiller dispersion.

Recently, new methods for preparing nanocomposites reinforced with carbon-based nanoparticles have been developed for materials with high filler contents, especially CNT, to serve specific applications [156], which include densification [214], spinning [215-216], layer-by-layer deposition [217] and pulverization [218].

1.4. Different morphologies and microstructures of nanocomposites from different carbon-based nanoparticles

1.4.1. Carbon black-filled polymer nanocomposites

The morphology study of nanocomposites can identify the interaction of the filler with the matrix, which strongly affects the properties of the final product. Scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), helium ion microscopy (HIM), transmission electron microscopy (TEM), etc., are the common instruments for morphology characterization of nanocomposites.

Generally speaking, the modification and functionalization of nanofillers improve their interaction with the matrix. The type of nanofiller, preparation process and host matrix are the other factors influencing the structure of the nanocomposites. Electrical conductivity of the material is highly dependent on the structure of the created conductive network throughout the nanocomposite. A study by Gubbels et al. [219] showed the improved electrical conductivity of PE/PS polyblend nanocomposite filled with CB by selectively localizing CB in PE. The opening size distribution of the PE phase and the specific interfacial area of the PE/PS blends have been extracted from the optical micrographs. In another study, the self-networking capability of CB in PLA was firstly confirmed using TEM, displaying the network structure of CB at the same 3 wt% loading in PLA matrix. For CB with low and medium self-networking capability, only some discrete clusters with a size of 100-500 nm were formed in the PLA matrix, while for CB with high self-networking capability, a continuous network structure was formed in the PLA [220].

1.4.2. Carbon nanotubes-filled polymer nanocomposites

As with other carbon-based nanocomposites, the stacked morphology and agglomeration of CNTs, alongside their size and dispersion level, can affect the properties of nanocomposites. For instance, analyses of FE-SEM images have addressed the size changes of CNTs depending on ball milling duration [221]. Another study used TEM to reveal that MWNTs more readily disperse within a PC matrix and have higher aspect ratios than SWNTs; extraction of the polymer from the composite prior to TEM imaging helped overcome the common issue of poor atomic contrast between the nanotubes and the organic matrix [222]. Additionally, morphology studies involving polarized Raman spectroscopy and wide angle X-ray scattering (WAXS) using synchrotron radiation showed reasonable levels of nanotube alignment.

In terms of evaluating the effects of functionalization and modification of the nanocomposites, SEM and TEM results can be used to compare the dispersion level of modified and pristine CNTs. In a study by Yuen et al. [223] SEM and TEM micrographs revealed that acid-modified MWNT and amine-modified MWNT were dispersed uniformly in a polyimide (PI) matrix, yet not improving the electrical conductivity of the material.

In terms of mechanical performance, morphology analysis can provide an insight about the matrix-filler interface. Functionalization of the fillers commonly improves bonding between filler surface and matrix. In a work by Paiva et al. [224] SEM micrographs showed an apparent good wetting of water-soluble PVA-functionalized nanotubes by the PVA matrix.

1.4.3. Graphene-based polymer nanocomposites

The exfoliation and diameter of incorporated graphene-based materials in a matrix can be addressed via morphology analysis using the techniques mentioned in the previous sections. A study of Li et al. [225] illustrated that expanded graphite presents a loosely bonded, porous and worm-like rod on a microscopic scale, which consists of nanoscopically parallel carbon sheets that are collapsed and/or deformed following an irregular pattern. In this study SEM micrographs showed that expanded graphite was exfoliated into individual and/or bundles of GnP through ultrasonication. TEM micrographs of these GnP after sonication suggested that the exfoliated graphene was formed by stacks of 10-15 graphene layers. Through post analysis of a controlled sonication process, the parameters including the duration, frequency and power could be tailored in order to avoid an excessive rupture of graphite, which would result in nanoparticles with lower aspect ratios and as a consequence probably lead to nanocomposites with reduced electrical conductivity.

Similar to CNTs, graphene can also benefit from surface functionalization to improve interaction with the matrix. Ramanathan et al. [226] claimed a better interaction of graphene with oxygen functionalities with polar polymers in comparison with unmodified SWNT and traditional expanded graphite, thereby imparting superior mechanical and highly enhanced thermal properties at exceptionally low loadings. The oxygen and hydroxyl functional groups on the functionalized graphene sheets are a great candidate for preparing composites with polar polymers such as PMMA, PAN and poly(acrylic acid) (PAA), giving rise to intimate nanosheet-polymer interactions and a percolated interphase essential to mechanical and thermal enhancement. Given these properties and the abundance of graphite, graphene-based fillers such as FGS or others have excellent potential to revolutionize the use of nanocomposites and enable their widespread use in large-scale applications [226].

Studies by Potts et al. [227] confirmed GO's exfoliation using mechanical stirring with much larger lateral dimensions and aspect ratio when compared to that of sonicated using atomic force microscopy (AFM). TEM and WAXS analyses are most likely the two most common means by which the state of dispersion can be assessed. Immiscibility of the phases and/or insufficient exfoliation of the graphite or GO-derived filler prior to mixing with polymer can result in large agglomerates consisting of stacked platelets when observed by TEM, which may also be suggested by the presence of a diffraction peak corresponding to the interlayer spacing of GO or graphite [227-228].

Small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS) measurements have been used on a variety of nanocomposite systems to detect the presence of fractal-like aggregates of filler at length scales beyond that of individual particles, although only limited information of this nature exists on GO-derived polymer composites [227, 229].

1.4.4. Polymer nanocomposites with nanohybrids

The unique electrical and mechanical properties as well as large surface area of graphene nanosheets have enabled them to be a new class of conducting materials for device, electrochemical and analytical applications. However, frequently used graphene fillers obtained from chemical reduction suffer from surface defects and readily form aggregated structures, greatly influencing their performance. Currently, improving the conductivity of graphene-based films and obtaining good control of architecture/property is an attractive topic for enhancing their application prospects. The use of CNTs to physically separate graphene stacks to preserve the high surface area of graphene and at the same time act as conducting carrier is an attractive and highly desirable idea [230-232].

A study undertaken by Yu and Dai [233] reported on the fabrication of large-area multicomponent hybrid films by sequential self-assembly of cationic polyethyleneimine functionalized graphene nanosheets and MWNTs forming hybrid carbon films with interconnected carbon structures of well-defined nanoscale pores. Therefore, this self-assembly method can be used to fabricate large-area multicomponent hybrid films with a well-defined architecture and tunable thickness on various substrates, suitable for electrochemical applications. More recently, Hong et al. [234] developed a layer-by-layer assembly technique for constructing transparent, flexible conducting hybrid multilayer thin films of MWNTs with rGO, which employs the electrostatic interactions of positively charged MWNTs and negatively charged rGOs. The obtained hybrid multilayer exhibited a significant increase of controllable electronic conductivity. Moreover, a more accurate control of the electrical conductivity was obtained for a hybrid system with vertical CNTs grown on reduced graphene films composed of overlapping and rGO platelets. Such carbon hybrid films have excellent flexibility and stretchability, can be readily transferred to any substrate, including non-planar surfaces, and were found to have ohmic electrical contacts throughout all junctions in the CNT/metal-catalyst/graphene-film system [235]. In another study, Fan et al. [236] managed the preparation of 3D CNT/graphene sandwich structures with CNT pillars grown within the graphene layers using chemical vapor deposition (CVD). The special structure endowed the high-rate transportation of electrolyte ions and electrons throughout the electrode matrix, resulting in excellent electrochemical performance of this hybrid material.

Recently, Van Thanh et al. [237] reviewed recent trends in the preparation and possible applications of hybrid thin films resulting from the combination of CNTs and graphene, which include applications such as transparent conductors, field-effect transistors or supercapacitors. Authors showed that in most cases these 3D CNT-graphene hybrid films displayed superior performances when compared to pristine GO, pristine graphene or even pristine CNTs.

2. EMI shielding theoretical models

2.1. Theoretical models based on electrical conductivity

2.1.1. Percolation models

Due to their inherently high mechanical performance and high electrical and thermal conductivities, carbon-based nanofillers (CNTs, nanosized CB, CNFs, graphene-based materials, etc.) have been vastly considered as a possible strategy to enhance the mechanical and/or transport properties characteristics of polymer nanocomposites, commonly resulting in final materials with multifunctional characteristics. Particularly, the extremely high electrical conductivity of carbon nanoparticles, reaching for instance values as high as 2×10^7 S/m for MWNTs [238], has generated a lot of interest in the field of conductive polymer materials, coming as a strategy to overcome the high cost and in many cases low thermal stability and relatively poor mechanical performance of common electrically conductive polymers [5]. In this sense, a lot of recent works have considered the modelling of the electrical conductivity and electrical behaviour of polymer nanocomposites containing different types of carbon nanoparticles, from the most common CNTs to the more recently considered graphene-based materials (monolayer/bilayer graphene, GnP, GO, rGO, etc.). Most of these studies are aimed to enhance the absolute value of electrical conductivity and/or minimize the critical concentration of carbon nanoparticles required to attain electrical conduction. Depending on its value and concentration dependence, this critical concentration may be related to specific conduction models, being the most common the so-called electrical percolation model [239-240], where electrical conductivity (σ) of the nanocomposite increases abruptly at a given nanoparticles concentration (the percolation threshold, ϕ_c), the polymer effectively passing from being insulating to electrically conductive, related to the formation of a conductive network by physical contact between conductive carbon-based nanofillers:

$$\sigma = \sigma_0 \left(\phi - \phi_c \right)^t, \text{ for } \phi > \phi_c \qquad (1)$$

In this equation σ_0 is a physical parameter commonly related to the intrinsic conductivity of the added carbon nanoparticles and t is the critical exponent that considers the dimensionality of the conductive system (for instance, $t = 2$ for a 3D direct-contact conductive network [241]).

A number of recent studies have considered the modelling of the electrical conductivity of polymer-carbon nanoparticles nanocomposites by considering carbon nanoparticles, especially CNTs, as random resistors dispersed throughout an insulating polymer matrix. Models have been developed based on the dimensionality of these random networks, from 2D [242-243] to 3D [244-245]. In the particular case of 3D models, a representative volume element (RVE) is taken as being representative of the polymer nanocomposite, meaning that its electrical conduction behaviour may be modelled by periodically repeating RVE (an example of a cubic-like RVE is presented in Figure 8(a)). However, many of these approaches disregard the interconnectivity of carbon nanoparticles, requiring RVEs with larger volumes. Additionally, most 3D models use simplified cubic RVEs and assume isotropic percolation of carbon nanoparticles in the matrix [244-246]. However, Shklovskii et al. [247] have demonstrated that in some cases, especially when dealing with high aspect ratio nanofillers such as CNTs or graphene, the conductive network may be anisotropic.

Fang et al. [248] have developed a model to describe CNT networks in polymer-CNT nanocomposites, accounting for electrical conductance of the CNT network across the boundary of adjacent representative volume elements, this way presenting a more realistic representation of the interconnectivity between nanotubes. Additionally, different RVE dimensions in different material directions were considered, this way exploring the possibility of anisotropic percolation, giving a more realistic vision of the structure-property relations of electrically conductive polymer-carbon nanoparticles system. A cubic-like RVE was considered in this work (see Figure 8(a)) with electric current being considered to propagate from the high voltage electrode to the low voltage one and CNTs assumed to have a rod-like geometry with interconnected conductive nodes (Figure 8(b)). Polymer nanocomposites' electrical conductivity was modelled, after considering the contribution of the interconnecting CNTs across the boundary surfaces of adjacent RVEs (see Figure 9), as follows:

$$\sigma = \left(2G_{rect} - 3G_{RVE}\right)\frac{L_x}{L_y L_z} \tag{2}$$

where G_{rect} is the electrical conductance of the rectangular parallelepiped shown in Figure 9, G_{RVE} is the equivalent conductance of the conductive network and L_{x}, L_{y} and L_{z} are respectively the edges of the cubic-like RVE in x, y and z axes (see Figure 9).

Figure 8

Figure 9

The effects of the orientation of the nanotubes on the percolation threshold and electrical conductivity were also studied, with the proposed model suggesting that perfectly random orientation of CNTs leads to lower threshold values, while high alignment along the direction of the electric current results in higher conductivity values at high CNT concentrations, as expected based on the formation of a conductive network by direct physical contact between the nanotubes [249].

2.1.2. Tunnelling-percolation models

Although the percolation threshold and percolation approaches have been vastly considered to model the electrical conductance behaviour of polymer nanocomposites containing conductive nanoparticles, classical percolation approaches have been found by many researchers to display a poor fit to most experimental results [250-252]. Other approaches, as tunnel-like conduction based models, such as Tunnelling Percolation

(TPM), and the Two Exponent Phenomenological Percolation Equation (TEPPE) based on the Generalized Effective Media (GEM) theory or even combined models, have been considered [253].

Tunnel conduction considers the possibility of electron transport between neighbouring conductive particles at very small gaps (a couple of nanometers), enabling modelling of the junction resistance between conductive nanoparticles and insulating matrix assuming a quantum tunnelling effect [254]. Nevertheless, as percolation threshold has to be taken into account, tunnelling-percolation models (TPM) have been considered, such as the one proposed by Rubin et al. [255]. In Hansen et al. [253], authors used a simplified Hertz distribution for particle distribution assuming a distance between conductors inversely proportional to the volume fraction of nanoparticles (ϕ) and directly proportional to the percolation threshold (ϕ_c):

$$\sigma \sim K\sigma_f \left(\frac{\phi - \phi_c}{1 - \phi_c} \right)^{t + \left(\frac{10\phi_c}{d\phi} - 1 \right)} \text{, for } \phi > \phi_c \tag{3}$$

where t is the critical exponent (see Eq. 1), d is the characteristic tunnelling distance of the system and K is a scaling correction factor that takes into account polymer tunnelling characteristics (a larger K factor is required for systems with larger tunnelling distances and higher percolation thresholds).

On the other hand, Generalized Effective Medium (GEM), an approach initially developed by McLachlan [256-258] and later extended to consider complex electrical behaviours [259] and expressed as the Two-Exponent Phenomenological Percolation Equation (TEPPE) [260-264], has been used to account for conductivity behaviours across the whole conductive particles concentration range, as it accounts for different behaviours below and above the percolation threshold according to:

$$\sigma = \sigma_p \left(\frac{\phi_c}{\phi_c - \phi} \right)^s \text{, for } \phi < \phi_c \tag{4}$$

$$\sigma = \sigma_f \left(\frac{\phi - \phi_c}{1 - \phi_c} \right)^t \text{, for } \phi > \phi_c \tag{5}$$

$$\sigma \cong \sigma_p^{\frac{t}{s+t}} \sigma_f^{\frac{s}{s+t}} \text{, for } \phi \sim \phi_c \tag{6}$$

where σ_p and σ_f are the direct current (dc) conductivities of the polymer and conductive filler, respectively.

As can be seen, these equations are the normalized standard percolation equations adapted, using exponents *s* and *t*, to each concentration range taking ϕ_c as reference.

Taking the best of both models, a combined TPM-TEPPE model was proposed by the authors, based on the GEM approach explicitly considering electron tunnelling above the percolation threshold, i.e., $\phi > \phi_c$ condition, as modelled by Rubin et al. [255].

Hansen et al. [253] demonstrated by modelling the electrical conductivity of several types of polymer-based systems reinforced with conductive nanostrands that the classical electrical percolation model as shown in Eq. 1 cannot distinguish between differences in the percolation limit across polymers, not lying within the proper region of conductivity (see Figure 10(a)). Also, the TPM model, though showing improved fit over the classical percolation model, underestimates to some extent its value (see Figure 10(b)), besides only modelling electrical conductivity for ϕ values above ϕ_c. This problem is solved by the TEPPE approach (see Figure 10(c)), which fits well in the regions of the percolation limit. However, the model does not fit so well at the percolation limit. Only when combining TPM and TEPPE models it was possible to have a proper fit across the whole concentration range (see Figure 10(d)), as separation analysis of the different concentration regions is strengthened by the inclusion of tunnelling approach (quantum tunnelling characteristics of the polymer matrix) above the percolation threshold.

Figure 10

Although significantly improving the modelling of the electrical conductivity of polymer-conductive nanoparticles nanocomposites by considering individual conductivity predictions for each nanoparticles concentration range, i.e., $\phi < \phi_c$, $\phi \sim \phi_c$ and $\phi > \phi_c$, and especially by incorporating the tunnelling-percolation approach to $\phi > \phi_c$ condition, the TPM-TEPPE model proposed by Hansen et al. [253] or similar approaches proposed by other authors still do not take into account the importance of interface effects. Recent studies have extended the analysis considering the importance of this conductor-insulator-conductor interface, as well as further characteristic tunnelling distance measurements and other quantum properties of the insulating matrix [265].

Wang et al. [266] have considered the modeling of the electrical conductivity of CNT-reinforced polymer nanocomposites by considering three main elements: the percolation threshold, approached by means of selecting an effective medium theory; possible interface effects, modeled by introducing an interfacial conductivity assuming a “thinly-coated” CNT; and tunneling-assisted interfacial conductivity, in order to take into account the possible influence of electron tunneling on interface conductivity. Particularly, the authors addressed tunnel-like conduction assuming a continuum medium of CNT network formation as a statistical process represented by Cauchy’s probability density function. As authors demonstrate, not considering the interface effect leads to overestimated electrical conductivities and not accounting for the additional tunnel-like contribution results in low predicted conductivity values beyond the percolation threshold. Furthermore, authors show that despite CNTs conductivity anisotropy, overall electrical conductivity is dominated by its axial component along CNT's direction:

$$\sigma_i^c = \frac{\sigma_i}{1+\rho(c_1)\cdot\sigma_i S_{ii}\left(1/\alpha+2\right)/R} \tag{7}$$

σ_i^c being the enhanced conductivity for the "coated CNT". This conductivity can be used to calculate the effective conductivity (σ_e) by replacing the value of σ_i^c in the following equation:

$$\frac{c_0\left(1-n_e\right)}{n_e+\left(1/3\right)\left(1-n_e\right)}+\frac{c_1}{3}\left[\frac{2\left(n_1-n_e\right)}{n_e+\left(n_1-n_e\right)S_{11}}+\frac{n_3-n_e}{n_e+\left(n_3-n_e\right)S_{33}}\right]=0 \tag{8}$$

which takes into account on the one hand the influence of CNT concentration (c_1), aspect ratio (α) and intrinsic conductivity (σ_i), and second of all the intrinsic interfacial resistivity (ρ), percolation threshold (here depicted as c_1^*), and the already mentioned probabilistic density parameter (γ), this way creating a continuum model that considers percolation by physical contact between CNTs, the interface effects, and tunnel-conduction.

Continuum model application was in good agreement with the experimental data of both MWNTs and SWNTs-reinforced PI nanocomposites [267-268], also showing how a not-fully perfect interface reduces the overall conductivity, while conduction by electron tunneling significantly increases its value after the percolation threshold.

Leon-Gil and Alvarez-Quintana [269] have developed a model for predicting the electrical conductivity of nanoresistors based on Landauer's tunnel conduction model [270-271]:

$$\sigma = \frac{2e^2}{h}\frac{T}{R} \tag{9}$$

where T is the transmission probability and R the reflection one.

As the transmission probability term gets very small assuming tunnel conduction and hence R is near 1, the above equation may be simplified to:

$$\sigma = \frac{2e^2}{h}T \tag{10}$$

where $2e^2/h$ describes the quantum unit of the electrical conductance and $T = \gamma e^{(-2kd)}$, being k the characteristic wave vector for tunnelling, d the distance between contacts and γ is determined by the characteristics of the electrodes.

In a similar way as with carbon nanotubes [266], Wang and co-workers [272-273] have considered the importance of the existence of an imperfect interface between nanoparticles and insulating matrix, as well as interfacial tunnelling taking into account the contribution of electron hopping between nanoparticles and using Cauchy's statistical function to predict increased tunnelling near the percolation threshold, on the electrical conductivity of graphene-based nanocomposites. Authors initially used a 2D model based on nanocomposites formed by distinct regions, one formed by graphene-rich aggregates, and a second one poor in graphene (matrix-dominant region). Overall conductivity, initially modelled considering these two regions, was then corrected taking into account the presence of the imperfect interfaces and tunnel conduction by using coated graphene or graphene aggregates instead of the original graphene layer or graphene aggregate.

Model application to experimental data of graphene-reinforced PS nanocomposites shows good accordance, in addition demonstrating that the percolation threshold for electrical conduction is determined by the dispersion of graphene nanoparticles and the aspect ratio of graphene aggregates, while, beyond percolation, overall conductivity is determined by the interface characteristics and the intrinsic conductivity of graphene and polymer matrix.

Feng et al. [265, 274] developed a mixed micromechanics model to predict the electrical conductivity of CNT-polymer nanocomposites assuming electron hopping and conductive networks as electrical conductivity mechanisms. Both interface layer and effective aspect ratio of CNTs were considered. Simulation results, which fitted well the experimental data for both single-wall and multi-walled CNT-polymer nanocomposites, seemed to indicate that both electron hopping and conductive networks contribute to the electrical conductivity, the second one becoming dominant with increasing CNT concentration. Interestingly, authors showed that the size of CNTs have a significant effect on the percolation threshold and hence on the overall electrical conductivity of the nanocomposites. Similarly, Ren et al. [275-276] and Cattin and Hubert [277] analyzed the piezoresistive response of CNT-reinforced polymer nanocomposites, showing how different nanoscale mechanisms influence the overall electrical conductivity and piezoresistive response through CNTs network, as mechanical deformation induced change in the distribution of CNTs can be well described by a strain-dependent conductivity exponent (mechanical deformation-related).

However, this work assumed a uniform random distribution of CNTs in the polymer, i.e., it did not assume the typical formation of CNT aggregates, promoted by their large aspect ratio and van der Waals surface attraction forces, nor the possibility of nanotubes being curved. As it is known, the electrical conductivity of polymer nanocomposites is highly dependent on nanofiller distribution and dispersion [278-279], as it has been shown that for low nanofiller concentrations the best results in terms of electrical conductivity are often reached by guaranteeing a combination of proper dispersion and relatively bad distribution of nanofillers, this way assuring physical contact between nanoparticles and the formation of a conductive network throughout the material (see Figure 11).

Figure 11

In this sense, Gong et al. have considered the CNT aggregation effect on the electrical conductivity modelling of polymer nanocomposites [280-281] and CNT deformation at nanotube junctions [282], showing that the smaller the size of CNT aggregates the closer the measured electrical conductivity of CNT-polymer nanocomposites to its theoretical limit. Additionally, authors demonstrated that CNT aggregation is the main reason behind the lower electrical conductivity of polymer-CNT nanocomposites than expected based on the theoretical values of both CNT and polymer matrix. Local deformation of CNT also plays a significant role in the electrical conductivity [282], as the intrinsic resistance in the deformed part of CNT near a CNT-CNT junction increases much faster than the decrease of CNT-CNT contact resistance at the same junction when two CNTs get closer, resulting in a net increase of resistance at the junction (see

Figure 12). Nevertheless, by using a multi-scale CNT percolation network model (see Figure 13), simulation predictions still showed some limitations previously overcame by assuming tunnelling besides percolative behaviour.

Figure 12

Figure 13

Several authors have applied the molecular dynamics simulation method to study the conductive properties of polymer nanocomposites containing carbon-based nanofillers [283-285]. Four factors were taken into account: polymer-nanoparticle interaction, grafting of nanoparticles, possible crosslinking of polymer molecules, and polymer blending. Authors show that conductivity variation is not linear regarding the mentioned factors. For instance, as interaction increases the dispersion of nanoparticles seems to first increase and then drop, while the conductivity increases monotonously.

2.1.3. Models for nanohybrids

The addition of hybrid conductive fillers, typically based on the combination of two or more types of carbon-based nanoparticles having different morphologies, has been recently considered as a possible strategy to enhance the electrical conductivity of polymer-based materials. In this sense, Chen et al. [286-287] have numerically studied using Monte Carlo simulation the electrical percolation of polymer-based nanocomposites containing CNT-CB hybrid nanofillers. By assuming CNTs as slender capped cylinders and CB nanoparticles as sphere-like aggregates (see Figure 14), authors found that on the one hand the addition of CB can decrease the required concentration of CNT for achieving percolation (especially when already close to the threshold with only CNT nanofiller) and on the other the percolation threshold may be significantly reduced by increasing the aspect ratio of the nanotubes, as well as increasing the diameter ratio of CB aggregates to CNTs, hence showing the synergistic effect of using both conductive nanofillers, corroborated by experimental studies. The nanocomposite percolation threshold ($\phi_c^{\mathrm{CB\&CNT}}$), defined as the volume fraction of both nanofillers when the electrical conductivity of the nanocomposites abruptly increases (threshold), was proposed by authors to be estimated using the following expression:

$$\phi_c^{CB\&CNT} = \phi_c^{CB}\left\{1-\left[1-\left(1-\frac{V_{CNT}}{\phi_c^{CNT}}\right)^{1.449}\right]^{d_{CNT}\Big/\left(0.622 d_{CNT}+0.0531 d_{CB}\right)}\right\}+V_{CNT} \qquad (11)$$

where ϕ_c^{CB} and ϕ_c^{CNT} are respectively the percolation concentration if only CB or CNT are present in the system, V_{CNT} is the volume fraction of CNT at the percolation threshold, and d_{CNT} and d_{CB} are respectively the diameter of the nanotubes and the diameter of CB aggregate (see Figure 14).

Figure 14

Similarly, Safdari and Al-Haik [288-289] proposed a model for predicting the electrical conductivity of polymer nanocomposites based on CNTs and GnP. They extended the model for polymer nanocomposites containing one single nanofiller to nanocomposites with hybrid nanofillers based on the combination of different nanofillers considering tunnelling conduction as the more effective mechanism for insulator-conductor transition, observing that enhanced electrical conductivities could be reached at lower total nanoparticles volume fractions, related to a positive synergistic effect between both conductive nanoparticles. Additionally, simulations revealed that the best system in terms of attaining the lowest possible electrical percolation threshold was the one that considered the addition of a minimum amount of a higher aspect ratio auxiliary nanofiller to a lower aspect ratio main one.

2.2. Electromagnetic interference shielding efficiency (EMI SE)

Conventional shielding materials include metals such as steel, copper or aluminium, which combine a high electrical conductivity and dielectric constant [290-292]. Nevertheless, they show some obvious disadvantages, such as high density, tendency to corrosion or even cost processing [293]. Most importantly, metals mainly protect from EMI by means of reflection, hence being out of use in applications where EMI absorption is required, as for instance in stealth technology [294-295]. Electrically conductive polymer composites could come as a possible alternative [296]. Among these, polymer nanocomposites containing carbon-based nanofillers have been gaining an increasing interest, especially in sectors such as electronics, automotive and aerospace [297-299], mainly due to their already demonstrated combination of high electrical conductivity and low percolation threshold.

EMI may be defined as a disturbance caused in an electronic system due to induced false voltage and current by the electromagnetic radiation generated from external sources [300]. Shielding from this electromagnetic radiation, which is emitted by computer circuits, cellular phones, electric motors, radio transmitters, etc., is hence required in order to protect electronic systems. This is done by attenuating the incident electromagnetic radiation by means of reflection, which requires free mobile charge carriers, and/or absorption, which happens due to mobile charge carriers and electric and magnetic dipoles within the material [301], though more commonly a combined reflection/absorption is used. An electromagnetic (EM) wave that strikes on a shielding material divides into a reflected wave, an absorbed wave, an internal reflected wave and a transmitted wave (see scheme presented in Figure 15).

Figure 15

The efficiency of a given material as electromagnetic attenuator can be expressed in terms of the electromagnetic interference shielding efficiency (EMI SE) [302-303]:

$$\text{EMI SE (dB)} = \text{SE}_\text{R} + \text{SE}_\text{A} + \text{SE}_\text{M} \tag{12}$$

where SE_R is the shielding efficiency due to reflection loss, SE_A is the shielding efficiency due to absorption loss and SE_M is the shielding efficiency due to internal reflection loss (secondary reflection). In most shielding environments SE_M has a very low value compared to the other two terms [304], and so EMI SE may be estimated as the sum of the reflection and absorption terms, i.e., $\text{EMI SE} \sim \text{SE}_\text{R} + \text{SE}_\text{A}$.

Assuming P_I (E_I), P_T (E_T) and P_R (E_R) as respectively the power densities of the incident, transmitted and reflected electromagnetic waves:

$$\text{EMI SE (dB)} = 10 \log\left(\frac{P_I}{P_T}\right) = 20 \log\left(\frac{E_I}{E_T}\right) \tag{13}$$

$$\mathrm{SE_R}\ (\mathrm{dB}) = 10\log\left(\frac{P_I}{P_R}\right) = 20\log\left(\frac{E_I}{E_R}\right) \tag{14}$$

Considering a two-port network system, the scattering parameters (S_{11} and S_{12}, and their reciprocals S_{22} and S_{21}) may be correlated to the reflection and transmission coefficients. Hence, reflection (R), transmission (T) and, as a consequence, absorption (A) shielding coefficients may be calculated according to [300]:

$$T = \left|\frac{E_T}{E_I}\right|^2 = |S_{12}|^2 = |S_{21}|^2 \tag{15}$$

$$R = \left|\frac{E_R}{E_I}\right|^2 = |S_{11}|^2 = |S_{22}|^2 \tag{16}$$

$$A = 1-(T+R) \tag{17}$$

Assuming multiple reflections as negligible leads to an effective absorption coefficient (A_{eff}) that can be described by the following equation [305]:

$$A_{eff} = \frac{1-(T+R)}{1-R} \tag{18}$$

where $\mathrm{SE_R}$ and $\mathrm{SE_A}$ are related to the reflection and transmission coefficients in the following way:

$$\mathrm{SE_R} = 10\log\left(\frac{1}{1\text{-}R}\right) \tag{19}$$

$$\mathrm{SE_A} = 10\log\left(\frac{1}{1-A_{eff}}\right) = \log\left(\frac{1-R}{T}\right) \tag{20}$$

Also, according to [306-307]:

$$\mathrm{SE_R}\ \text{(dB)} = 20\log\left[\frac{\left(\dfrac{\sigma_{\mathrm{ac}}}{\omega_{\mathrm{H}}\varepsilon_0\mu_r}\right)^{1/2}}{4}\right] \tag{21}$$

$$\mathrm{SE_A}\ \text{(dB)} = 20\log\left[\exp\left(\frac{t}{\delta}\right)\right] \tag{22}$$

where σ_{ac} is the ac electrical conductivity, ε is the dielectric permittivity, $\delta = \left(2/\omega_{\mathrm{H}}\mu\sigma_{ac}\right)^{1/2}$ is the depth of radiation penetration in the material, μ is the magnetic permeability of the polymer nanocomposite, μ_{r} the relative permeability of the shielding material ($\mu_{\mathrm{r}} = 1$), and $\omega_{\mathrm{H}} = 2\pi f_{\mathrm{H}}$, where f_{H} is the radiation frequency in MHz.

2.3. Parallel resistor-capacitor model

Several authors have demonstrated by using a parallel resistor-capacitor model (see scheme embedded in Figure 16(a)) that the ac electrical conductivity (σ_{ac}) of nanocomposites, usually measured at microwave frequencies such as the X-band (8.2-12.4 GHz), may be taken as a good predictor of their EMI SE, with EMI SE increasing almost linearly with σ_{ac} (see Figure 16(b)) [308]. Also, σ_{ac} has been seen to vary linearly with the concentration of added carbon nanoparticles, being higher than σ_{dc} even below the percolation threshold. Electrical conductivity has been found to be frequency-dependent, and can easily be understood by using a simple parallel resistor-capacitor model, with conductive carbon nanoparticles contributing to electrical resistance and the insulating polymer matrix contributing to ac conductance.

Figure 16

It has been shown in the literature that the addition of small amounts of high aspect ratio conductive nanofillers to polymers, such as CNTs or graphene, results in polymer nanocomposites with enhanced electrical conductivity and as a consequence high EMI shielding efficiency [301, 309-312]. As these nanofillers are highly conductive, increasing their aspect ratio leads to longer conductive pathways within the insulating polymer matrix, enhancing electrical conductivity (see comparison between high aspect ratio and lower aspect ratio fillers presented in Figure 17).

Figure 17

Theilmann et al. [301] showed that, while for electrical conductivity in direct current conditions (σ_{dc}) physical connectivity between CNTs was required, EMI SE and σ_{ac} did not require it [313-314], as high frequency EM waves may couple between neighbouring CNTs. Nevertheless, as EMI SE and σ_{ac} are still dependent of physical contact between CNTs, maximization of the connectivity through improved CNT separation and dispersion throughout the insulating matrix is still a requirement [310, 315] (compare Figure 17(b) and (c) with (a), as separated and well-dispersed CNTs are more likely to physically touch and form conductive paths). Nanofiller alignment, especially in those cases where nanofillers have a platelet-like (such as graphene) or a fibre-like geometry (such as CNTs), also affects the values of electrical conductivity and as a consequence EMI SE. Nanoparticle alignment reduces the probability of contact, hence being easier to attain an interconnected network with longer conductive pathways under random nanofiller orientation (compare Figure 17(b) and (c)) [310, 315].

2.4. Multiscale hybrids

Multiscale hybrids based on the combination of highly reflective and highly absorptive EM materials have been recently considered for EMI shielding applications. For instance, Huynen and co-workers [316-317] have considered a CNT-reinforced polymer foam, characterized by its high EM absorption, inserted into an aluminium honeycomb, characterized by its high EMI shielding due to reflection, hence combining a low dielectric constant (as close as possible to 1) with a moderately high absolute electrical conductivity (around 1 S/m at the high frequencies required in EMI shielding, which can be attained by adding low amounts of conductive nanoparticles such as CNTs to polymers [318-319]) in one single material (see Figure 18). As the dielectric constant is increased as a consequence of adding CNTs, detrimental in terms of EM reflection, authors considered the strategy of using a polymer foam, which, due to its particular cellular structure, globally reduces the dielectric constant, resulting in a nanocomposite with a dielectric constant close to that of the polymer without nanotubes and an electrical conductivity close to the optimum region for EMI shielding [320]. Interestingly, authors demonstrated the possibility of tuning the EM absorption frequency by modifying the initial shape of the metallic honeycomb, as EM propagation inside each cell of the honeycomb is directly affected by the metallic walls of the cell, the problem being similar to that of a metallic waveguide filled with a material of known complex permittivity, the propagation constant becoming dependent on the width (a) and the height (b) of the waveguide. For instance, for rectangular cells and thus waveguides (see Figure 19), the complex propagation constant (γ) may be determined by the following expression:

$$\gamma = j\sqrt{\varepsilon_{eff}\,\frac{\omega^2-\omega_0^2}{c_0^2}} = j\sqrt{\varepsilon_{eff}\,\frac{\omega^2}{c_0^2}-\left(\frac{m\pi}{a}\right)^2-\left(\frac{n\pi}{b}\right)^2} = \sqrt{\gamma_c^2+\left(\frac{m\pi}{a}\right)^2+\left(\frac{n\pi}{b}\right)^2} \qquad (23)$$

Figure 18

Figure 19

The insertion of a metallic honeycomb into the CNT-reinforced polymer foam further reduced the real part of the effective dielectric constant, with the honeycomb effectively acting reducing the reflected power, hence the hybrid displaying a lower effective dielectric constant than the nanocomposite foam by itself.

3. EMI shielding behaviour of carbon-based polymer nanocomposites

3.1. Influence of the electrical conductivity

Improved dispersion of CNTs has been addressed in several works, as it has been shown that proper nanotube distribution and dispersion is crucial in terms of forming an effective conductive network, minimizing the percolation threshold and maximizing the absolute electrical conductivity. Different approaches have been considered, particularly the improvement of dispersion during processing, functionalization and surface modification of the nanotubes (as a way to avoid nanotube aggregation) and selective nanotube dispersion.

3.1.1. Effect of nanoparticle dispersion by means of processing

In terms of improving dispersion during processing, Espinosa-Martínez et al. [321] analyzed the influence of the cooling rate during melt-compounding by twin-screw extrusion in the morphological, structural and electrical properties of PEN-MWNT nanocomposites, showing that the addition of increasingly higher concentrations of MWNTs promoted PEN crystallization during cooling, leading to electrical conductivities in the range of semiconductors (around 10^{-4} S/cm), which authors related to the formation of an interconnected nanotubes network throughout the crystalline structure formed in PEN nanocomposites.

Huang at al. [322] were able to prepare PA11-MWNT nanocomposites with enhanced dielectric properties and electrical conductivities using a conventional melt-compounding process. The uniform dispersion of MWNTs throughout PA11's matrix guaranteed during melt-mixing induced the crystallization of PA11 when quenching from the melt, which, together with MWNTs, helped enhancing the dielectric properties and electrical conductivities (reaching values as high as 10^{-3} S/m for 2.5 vol% MWNT) of the nanocomposites by forming nanocapacitors within the nanocomposites and the interfacial polarization effect resulting from the accumulation of charge carriers at the interfaces between the nanotubes and PA11.

Melt-mixed HDPE-MWNT nanocomposites processed by compression-moulding and blown film extrusion were investigated in terms of their structure and properties by Xiang et al. [323]. Although authors demonstrated that blown film nanocomposites exhibited better mechanical performance due to improved orientation and disentanglement of MWNTs during processing, also, as a consequence, higher blow-up ratios (BURs) led to the destruction of the conductive pathways formed by the nanotubes and thus to nanocomposites with lower electrical conductivities (higher resistivities), which they related to a distance between nanotubes that exceeded the maximum critical distance for electron hopping (around 1.8 nm [324]). Interestingly, authors demonstrated that these conductive pathways could be partially restored using a controlled annealing process of the blown nanocomposite films by facilitating the reformation of local contacts between nanotubes and MWNTs partial reaggregation, showing that at a concentration of MWNTs of 8 wt% it was possible to maintain a conductive network even at high BURs.

Fogel et al. [325] used a three-roll mill procedure to prepare MWNT-reinforced epoxy nanocomposites and obtained a percolation threshold around 0.25 wt% MWNT and an electrical conductivity of 10^{-2} S/m for an MWNT concentration of 0.75 wt%. This percolation threshold, only slightly above some of the lowest percolation thresholds found in the literature for this type of system (mechanically-dispersed nanotubes in an epoxy matrix) [326-327], was related to the formation of a quite homogeneous 3D nanotube network.

Wang and co-workers [328] prepared PI-MWNT nanocomposite films by in-situ polymerization using a diamine as both comonomer as well as non-covalent dispersant of the nanotubes through π-π interaction. Direct result of the good dispersion of MWNTs achieved in solution as well as polymer matrix, electrical conductivity increased at 0.50-0.75 wt% MWNT, reaching promising values of 6.8×10^{-7} S/cm at 0.75 wt% MWNT, showing that non-covalent dispersant may improve the affinity of polymers to nanotubes (and it is expected to be similar with other carbon-based nanofillers) and thus may be useful in the development of polymer nanocomposites with enhanced functionalities, such as high electrical conductivity.

Singh et al. [329] developed PU-MWNT nanocomposite thin films with enhanced dielectric properties using a solution grown method. As a result of a proper dispersion of the nanotubes throughout the PU matrix, facilitated by using an initially liquid system, the resulting nanocomposites displayed enhanced electrical conductivities with a characteristic percolative behaviour.

Wang and co-workers [330] analyzed the electrical conductivity of nanocomposites based on MWNTs and phthalocyanine polymer prepared by thermal annealing. The addition of the nanotubes and the elevated annealing temperatures (from 300 to 500 ºC) endowed the nanocomposites with high electrical conductivity. Particularly, the combination of the highest annealing temperature (500 ºC) and addition of 5 wt% MWNTs led to nanocomposites with an electrical conductivity of around 10^{-3} S/cm, much higher than that of the unfilled polymer and approximately 7 orders of magnitude higher than that of the nanocomposites annealed at 300 ºC, showing the synergistic effect between processing (thermal annealing) and the addition of the conductive CNTs.

Similar results have been found when using graphene or graphene-based materials [331-333]. Jan and co-workers [331] considered the preparation of TPU nanocomposites containing high aspect ratio graphene nanosheets, GNS (up to a graphene concentration of 0.55 vol%), previously prepared by liquid exfoliation, and showed that, result of the homogeneous dispersion of said nanosheets within the TPU matrix the nanocomposites displayed conductivities that were 10 to 1000 times higher and dielectric constants 5 to 6 times higher at 100 Hz when compared to the unfilled TPU. The authors related these spectacular increases to interfacial and orientation polarization effects directly resulting from the well-exfoliated and dispersed GNS.

Zhong et al. [333] used ultrasonication to enhance the dispersion of various graphene-based materials, particularly, untreated graphite and expanded graphite in PEI, and observed that, while ultrasonication showed little effects in changing the electrical properties of PEI nanocomposites containing the untreated graphite, PEI nanocomposite with 5 wt% of expanded graphite displayed a reduction in the electrical volume resistivity of almost 3 orders of magnitude and a lower percolation threshold, which authors related to a large particle size and partial aggregation of untreated graphite particles within the PEI matrix.

Recently, Sundararaj and co-workers [334-335] have shown that, in order to have a proper quantification of the dispersion state of the nanofiller throughout the polymer matrix after nanocomposite preparation and thus proper assessment of the effect of dispersion on the formation of an effective electrically-conductive network, TEM analysis needs to be coupled with additional techniques, namely optical microscopy (OM) and atomic force microscopy (AFM), the coupling of the three techniques enabling a multiscale image of the dispersion state of the nanofiller. For instance, they have shown that the addition of carbon nanotubes synthesized at a temperature of 650 ºC and having a combination of high carbon purity, high aspect ratio and high crystallinity to a PVDF matrix led to a better micro-dispersion (assessed by OM) and nano-dispersion (assessed by TEM) states within the polymer when compared to CNTs synthesized using different conditions, comparatively resulting in nanocomposites with significantly lower percolation thresholds (0.3 wt% CNT) and higher electrical conductivities (maximum of 22 S/m at 3.5 wt% CNT), as well as higher EMI SEs (16.7 dB at 3.5 wt% CNT).

3.1.2. Effect of nanoparticle functionalization and/or surface modification

Functionalization and surface modification of the nanotubes has also been considered in the literature as a strategy to avoid nanotube aggregation and thus improve nanotube dispersion within polymers [335-339]. In this sense, Ayesh et al. [340] have recently considered the addition of hydroxynaphthoic acid (HNA) to MWNT-PS nanocomposites having a fixed concentration of nanotubes of 0.85 wt%. The authors observed that there was an effective improvement of the dispersion of the nanotubes and of the interfacial bond in the HNA-MWNT-PS nanocomposites up to the addition of 1 wt% of HNA, as HNA favoured the formation of an MWNT conductive network and as a result led to enhanced electrical conductivities (around 3 orders of magnitude higher when compared to the unfilled polymer).

Jang et al. [341] analyzed the influence of MWNT modification on the electrical properties of PC-PLA blend nanocomposites. Particularly, the authors surface-modified MWNTs by grafting lactic acid (LA-g-MWNT), this way compatibilizing the nanotubes with PLA present in the polymer blends (see scheme of MWNT surface modification in Figure 20(a)). As a result of the improved compatibility of the nanotubes with the PLA phase (dispersed phase) due to the chemical modification of MWNT grafting lactic acid, PC – PLA – LA-g-MWNT nanocomposites displayed increased electrical conductivities (as high as $\approx 10^{-1}$ S/cm at a MWNT concentration of 1.0 phr of polymer), as there was an increased connectivity of the MWNT-MWNT network structure.

Figure 20

Wang et al. [342] prepared by solution blending oleic acid-modified MWNT-reinforced PS nanocomposites and observed that the surface modification of the CNTs with oleic acid via covalent bonding between hydroxymethylated MWNT and the long-chained molecules of oleic acid in xylene (see scheme presented in Figure 20(b)) guaranteed a proper dispersion of the nanotubes throughout the PS matrix and as a consequence led to nanocomposites with enhanced electrical conductivities, the nanocomposites showing a transition from insulating to conductive at about 1.5 wt% modified MWNTs (percolation threshold) and a maximum electrical conductivity of about 3×10^{-4} S/cm at 3.0 wt% modified MWNTs.

Zhang et al. [343] proved that the addition of low CNT content, when prepared by coating the nanotubes on the surface of gelated/swollen soft PP pellets, promoted the formation of electrically-conductive PP-CNT nanocomposites with a low percolation threshold (0.3 wt% CNT - $\sigma \approx 10^{-2}$ S/cm) and a high electrical conductivity (as high as 10^{-1} S/cm with only adding 2 wt% CNT). This remarkable electrical conductivity was attributed to the formation of an effective conductive CNT network at a low temperature of compression (120 ºC), as at this temperature PP pellets coated with CNTs almost did not deform and hence did not break the coating layer of CNTs, which were pressed together forming the conductive network.

Tan et al. [344] proved that different proportions of functionalized MWNTs and functionalized graphene dispersed throughout a poly(styrene-b-butadiene-b-styrene) (SBS) matrix led to nanocomposites with enhanced electrical conductivities, with maximum improvement attained at 50/50 nanofiller weight ratio (total: 1.5 wt% of each nanofiller).

A recent review has been presented by Kaseem and co-workers about the fabrication and resulting properties of PS composites containing CNTs [345]. In this review the authors discuss the non-covalent and covalent modifications of CNTs and their later addition to PS, focusing on the improved dispersion of the nanotubes and enhanced compatibility with PS in the resulting nanocomposites, ultimately leading to nanocomposites with higher electrical conductivities at lower CNT concentration, hence extending their industrial applicability.

Similarly, Zarate-Triviño and co-workers [346] analyzed the effect of MWNT functionalization on the electrical behaviour of MWNT-chitosan nanocomposite films. Contrarily to most works, the authors showed that the strong interaction due to hydrogen bonding between the chitosan matrix and hydroxylated-modified MWNTs led to nanocomposites with higher electrical resistivities, i.e., lower electrical conductivities (films showing a typical insulating behaviour), while the addition of unmodified MWNTs resulted in nanocomposites which displayed a characteristic percolative behaviour at a CNT concentration of 4 wt%, reaching a maximum electrical conductivity of around 10^{-2} S/cm at 15 wt% MWNT. These results demonstrate the importance of controlling surface modification/functionalization of CNTs in order to guarantee proper nanotube dispersion within the polymer matrix and avoid excessive interaction with said matrix, always with the objective of forming an effective conductive network.

As with CNTs, graphene, GO, rGO or GnP have been surface-modified and/or functionalized in order to regulate the electrical properties of polymer nanocomposites. In this sense, Qian et al. [347] have functionalized GO nanosheets, particularly using 3-aminopropyltriethoxysilane as modifier, and considered their use in the in-situ polymerization of PI-based nanocomposites for enhancing their electrical properties. As the functionalized nanosheets exhibited good dispersibility and compatibility with the PI matrix due to strong interfacial covalent interactions, the resulting nanocomposites displayed electrical conductivities at 1.5 wt% functionalized graphene that were 10 orders of magnitude higher than that of the insulating unfilled PI (2.63×10^{-3} S/m).

Similarly, Sefadi and co-workers [348] improved the dispersion of expanded graphite nanosheets in an EVA matrix by previously surface-modifying them with sodium dodecyl sulphate (SDS) and later on subjecting the melt-blended nanocomposites to electron beam irradiation. Nanocomposites containing the SDS-modified expanded graphite showed better interfacial adhesion than their non-modified expanded graphite nanocomposites counterparts. As a result of this too strong interfacial adhesion, SDS-modified expanded graphite nanocomposites displayed extremely low values of electrical conductivity (much lower than the nanocomposites containing the non-modified graphene) and much higher electrical percolation thresholds, hence showing that an excessive interaction between matrix and conductive nanofiller(s), especially in those cases where there is not a good balance between nanofiller distribution and dispersion, can be counterproductive in the formation of an effective conductive network.

In this sense, Santos and co-workers [349] used as-received and chemically-modified GnP, the last ones PP-functionalized using PP-g-MA, to create by one-step melt-mixing PP nanocomposites. Although intensive mixing enabled to disperse GnP in both cases, the stability of the dispersion after melt-blending could only be guaranteed by using the modified and functionalized nanoplatelets, delaying re-agglomeration due to stress relaxation of the polymer melt. As chemically-modified nanoplatelets were also functionalized before melt-mixing it was possible to improve their interfacial interaction with the polymer matrix, leading to final nanocomposites with enhanced electrical conductivity. Park et al. [350] reached similar conclusions in the case of PE-graphene composites, as the non-polar nature of PE, as with PP, required the prior chemical functionalization of graphene in order to guarantee its proper dispersion throughout the polymer matrix and thus proper enhancement of the electrical conductivity, a 10^6-fold reduction in electrical resistance regarding the pure PE being observed, much higher than composites containing similar amounts of unmodified graphene.

3.1.3. Effect of nanoparticle selective dispersion

A recent strategy to enhance the electrical conductivity of CNT-reinforced polymer nanocomposites has considered the selective dispersion of CNTs in a particular polymer phase. For instance, Bera et al. [351] prepared polymer nanocomposites with high electrical conductivities and low percolation thresholds (around 2.5×10^{-2} S/cm at 0.15 wt% MWNT) by selectively dispersing MWNTs in PCL through solution blending and adding PCL beads into this solution, this way effectively creating an interconnected MWNT-MWNT conductive network throughout the solution blended region (see scheme showing the selective dispersion of MWNT in PCL-MWNT nanocomposites presented in Figure 32, section 3.2.3.). The same research group [352] extended this idea by selectively dispersing a conductive bi-filler consisting of MWNTs and expanded graphite in HDPE and using this nanocomposite as minor phase in a PMMA nanocomposite, reaching an electrical percolation threshold as low as 0.07 wt% MWNT resulting from the formation of a highly effective MWNT-EG-MWNT conductive network in the well dispersed HDPE throughout the PMMA matrix.

Gao et al. [353] prepared and analyzed the dielectric properties of PEEK-PI-MWNT nanocomposites by selectively distributing and dispersing the nanotubes in one of the polymer phases, in this case PI. The authors considered the concept of double percolation by varying the ratio of PEEK-PI blends and keeping constant the amount of MWNTs, with nanocomposites with a co-continuous phase exhibiting higher electrical conductivities, and later keeping constant the proportion of PEEK and PI in the blends and changing the concentration of MWNTs in the PI phase, once again the formation of a co-continuous polymer phase up until an amount of 2 wt% MWNT favouring a higher electrical conductivity (see scheme in Figure 21 showing the microstructural evolution of PEEK-PI-MWNT blends with increasing the amount of PI and keeping a concentration of 1 wt% MWNT).

Figure 21

Similarly, Nasti et al. [354] generated a double percolated morphology in which PS, percolated by the prior addition of 2 wt% MWNTs, percolated a PLA phase. Authors showed how this strategy promoted a bicontinuous morphology with a high selective localization of MWNTs (in this case in the PS phase), facilitating the control of the dispersion of these conductive domains and hence allowing to diminish the electrical percolation threshold to a value as low as 0.45 vol% MWNT on total volume.

Moud et al. [355] selectively distributed and dispersed CNTs in PA6 phase in PA6-PP polymer blends and compared the electrical conduction behaviour with that of PA6-CNT nanocomposites where the nanotubes were randomly distributed (see micrographs presented in Figure 22). Due to the good interaction and interfacial compatibility to PA6 and in contrast poor interaction with PP, carbon nanotubes were almost fully localized and evenly distributed and dispersed in the PA6 phase in PA6-PP polymer blend nanocomposites, creating an effective conductive network that resulted in electrical conductivities that were 3 to 7 orders of magnitude higher than that of unfilled PA6.

Figure 22

Otero-Navas et al. [356] have investigated the effect of CNTs on the broadband dielectric properties of PP-PS blends, showing that the selective localization of said CNTs at the interface and inside the PS phase in both co-continuous as well as PP-rich blends led to an improved conductive network and decreased the amount of PS-CNT phase needed to percolate in PP phase. Particularly, CNTs located at the interface of both PS and PP phases acted bridging CNT-rich PS phases dispersed throughout PP's phase, double percolation, primary in CNT-rich PS phase and secondary through bridging said phases throughout PP's phase, being observed with increasing the concentration of nanotubes. While for low amount of CNT-rich PS phase the dispersed conductive domains did not guarantee interconnectivity and hence led to materials suitable for charge storage applications, co-continuous blends allowed interconnectivity between CNT-rich PS domains, thus materials finding applications for EMI shielding.

Contrarily to Gao et al. [353], the same research group [357] has recently shown that the selective localization of CNTs in PA6 in PS-PA6 blends, once again related to the higher interaction of CNTs with PA6 when compared to PS, worked better in terms of maximizing the electrical conductivity of the resulting nanocomposites at high CNT loadings if the CNT-rich PA6 was in the form of dispersed droplets throughout the PS matrix (i.e., if PA6-CNT phase was in a much lower amount) rather than co-continuous one (50/50 proportion of PA-CNT and PS phases). For example, for a high CNT concentration of 3.5 phr, the electrical conductivity of 90 PS/10 PA6 blend resulted 4 orders of magnitude higher than the co-continuous 50 PS/50 PA6 blend. Once again, a double percolation mechanism was given as explanation, as a primary percolation occurred by the selective localization and dispersion of CNTs in PA6 phase, and a secondary one by the electrical bridging of excess CNTs localized in PS phase (see Figure 23).

Figure 23

Similarly, Nair and co-workers [358] were able to reduce the rheological percolation threshold, directly related to the electrical threshold, in PP-natural rubber (NR) blends containing MWNTs by selectively localizing the nanotubes in the NR phase. The authors observed that even at low NR contents the local concentration of MWNTs in the dispersed NR phase was enough to guarantee the formation of an effective percolative network with bridging of some MWNTs from the NR phase to the PP continuous phase. At higher NR proportions (50PP-50NR), a double percolation behaviour was observed, the MWNTs forming a percolation network inside the already continuous NR phase.

In this sense, Patra et al. [359] were able to reduce the electrical percolation threshold of MWNT-reinforced nanocomposites based on PS-LDPE blends (to a value as low as 0.21 wt% MWNT) by selectively dispersing the nanotubes in the LDPE phase in the cases where LDPE was the minor phase in the blend, the high electrical conductivity values (around 10^{-4} S/cm at 0.5 wt% MWNT and about 10^{-3} S/cm at 1 wt% MWNT, in both cases for a 70 wt% PS-30 wt% LDPE blend) being explained by a tunnel-like mechanism.

Farahani et al. [360] considered the heterogeneous distribution of conductive MWNTs during processing of bi-phasic polymer blends as strategy to enhance the electrical conductivity of nanocomposite films, with bi-phasic nanocomposite films with a heterogeneous distribution of nanotubes presenting electrical conductivities (around 2.2×10^{-3} S/cm) that were about two orders of magnitude higher than those corresponding to nanocomposites containing homogenously distributed MWNTs ($\approx 3.3 \times 10^{-5}$ S/cm), in both cases for a MWNT concentration of 1 vol%.

Very recently, Biswas and co-workers [361] presented a review that highlights recent advancements in bi-phasic polymer blends with selective localization of conductive nanomaterials thought for EMI shielding applications, concluding that selective localization and dispersion of conductive nanoparticles reduces the electrical percolation threshold, offer more possible interfaces that facilitate multiple internal reflection of EM waves, and enable the tailor distribution of conductive nanomaterials favouring the formation of an interconnected conductive network throughout the matrix.

3.1.4. Effect of nanoparticle’s aspect ratio

Alongside the already mentioned strategies to enhance the dispersion of CNTs throughout polymer matrices in order to improve electrical conductivity, the influence of the aspect ratio of said nanotubes has also been considered in the literature. As an example, Verma et al. [362] studied the effect of adding long and short MWNTs (respectively named l-MWNT and s-MWNT), i.e., nanotubes with very different aspect ratios, in the case of the long MWNTs between 1356 and 1937 and in the case of the short ones around 158, into a random PP copolymer using a twin-screw extrusion melt recirculation approach. Direct consequence of the melt recirculation used during blending the resulting nanocomposites displayed good nanotube dispersion, with a low percolation threshold being attained for both the nanocomposite containing l-MWNT (percolation threshold of 0.45 wt%) as well as the one containing s-MWNT (percolation threshold of 1.07 wt%), reaching a maximum electrical conductivity between 10^{-3} S/cm (s-MWNT) and 10^{-2} S/cm (l-MWNT). As can be seen, as both types of nanocomposites showed a proper nanotube dispersion, the lower percolation threshold and higher electrical conductivity of the nanocomposite containing l-MWNTs was primarily attributed to the higher aspect ratio of l-MWNTs, as this higher aspect ratio led to a higher probability of formation of an effective conductive network throughout the polymer at the same concentration of nanotubes. As will be seen in the next section, as a result of their higher conductivity, nanocomposites with l-MWNTs also displayed higher EMI shielding efficiencies.

Shezhad et al. [363] mixed in different relative concentrations two types of carbon nanotubes having different aspect ratios (CNT-1, with a diameter of 10-30 nm, and CNT-2, with a diameter of 20-40 nm, in both cases having a length of 5-15 μm) and melt blended them with a PP-based thermoplastic elastomer, showing that it was possible to tune the electrical percolation characteristics by changing the relative concentrations of CNT-1 and CNT-2 towards the development of high efficient pressure sensors.

Several authors have also analyzed the influence of the aspect ratio of graphene-based materials on the electrical conduction properties of nanocomposites. Wang et al. [364] studied the electrical conduction behaviour of syndiotactic PS-based nanocomposites containing two types of graphene nanosheets having different thicknesses (average thicknesses of 2 nm and 50 nm) and thus different aspect ratios. The authors observed that the aspect ratio played a key role in the electrical percolation threshold, as nanocomposites containing graphene nanosheets with the higher aspect ratio (lower thickness of 2 nm) showed a much lower threshold (0.46 vol% graphene) than those containing the thicker graphene nanosheets (3.84 vol% graphene). Similarly, although varying the lateral dimension of graphene nanosheets instead of their thickness (50 and 500 μm), Paszkiewicz et al. [365] showed that the addition of the nanosheets having the higher aspect ratio (smaller lateral dimension) to poly(trimethylene terephthalate) (PTT) resulted in conductive nanocomposites at 0.3-0.5 wt% graphene, while graphene flakes having a higher lateral dimension of 500 μm did not lead to conductive nanocomposites, which was related to a combined effect of their higher aspect ratio and more uniform distribution within the PTT matrix.

Sabzi et al. [366] added two types of GnP into PLA through solvent mixing and showed that while one of the graphenes having a thickness of less than 1 nm was fully exfoliated and homogeneously dispersed in the PLA matrix (see Figure 24(a) and (b)), GnP (average thickness of about 10 nm) were poorly dispersed with aggregates formed by stacks of graphene layers (see Figure 24(c) and (d)). The electrical conductivity of PLA increased in both cases in more than 12 orders of magnitude up until 0.1 S/m, as both types of graphene led to the formation of conductive paths in the polymer matrix. Comparatively, the addition of graphene with the lower thickness and hence higher aspect ratio (around 10000) resulted in nanocomposites with lower percolation thresholds (0.7 wt%, when compared to 7.7 wt% GnP), once again related to a combination of the higher aspect ratio of graphene and, as can be seen in Figure 24, its more homogeneous dispersion in the polymer matrix.

Figure 24

In their review dedicated to the electrical percolation in carbon nanotube polymer nanocomposites, Bauhofer and Kovacs [367] showed the viability of using the concept of excluded volume to estimate the electrical percolation threshold of nanocomposites containing dispersed non-spherical particles, which would enable this method to be used also with GnP. As indicated by its name, the excluded volume concept relates the percolation threshold not with the true volume of the nanofillers but instead to their excluded volume. Once nanofiller particles are homogeneously distributed and dispersed, which authors assumed to be a statistical percolation, the percolation threshold resulted inversely proportional to the aspect ratio of the nanofiller, comparatively spherical nanoparticles having a much lower aspect ratio than non-spherical nanoparticles (such as tubular-like CNTs or platelet-like graphene) displaying much higher electrical percolation thresholds. This theoretical approach is in good agreement with the previously shown experimental results, as well as with the theoretical models presented in section 2.

3.1.5. Effect of the use of nanohybrids

The use of nanohybrids based on the combination of carbon nanotubes and other nanofillers has also been recently considered. Tsonos and co-workers [368] considered the addition of nanohybrids based on carbon nanotubes and magnetite (Fe_3O_4) nanoparticles into PVDF with the objective of creating multifunctional nanocomposite films with improved transport properties. Particularly, the authors considered the addition of magnetic Fe_3O_4 nanoparticles into nanocomposites with a concentration of nanotubes already clearly above the percolation threshold, demonstrating that the resulting nanocomposites not only displayed a ferromagnetic behaviour but also showed a gradual increase of the electrical conductivity with increasing the amount of magnetite up until 10 wt% Fe_3O_4 (electrical conductivity of 2.8×10^{-4} S/cm, more than two orders of magnitude higher than that of equivalent PVDF-CNT nanocomposites without magnetite).

In the same way, Zakaria et al. [369] introduced carbon nanotube-alumina (CNT-Al_2O_3) nanohybrids chemically synthesized via chemical vapour deposition into an epoxy-based system and showed that the resulting nanocomposite displayed a more homogeneous nanohybrid dispersion than the equivalent physically mixed epoxy-CNT-Al_2O_3 system, some filler aggregation being observed in this case, and, as a consequence, the nanocomposite containing the chemically synthesized nanohybrids had a higher electrical conductivity and a higher dielectric constant, with an enhancement of around 20% when compared to the unfilled epoxy.

3.1.6. Effect of nanoparticles/nanohybrids alignment

As it has been shown, carbon-based nanofiller hybrids combined with different types of polymers are excellent candidates for a broad range of applications, from thermal management to energy storage. Nevertheless, said applications depend on their performance and thus a precise control of their microstructure is of crucial importance. As electrical conduction is highly dependent on the formation of an effective conductive network between carbon nanofillers, the main efforts have been done towards guaranteeing physical contact between the nanoparticles. One of the current strategies considers the alignment of conductive nanofillers or nanohybrids to form “chain” connections by means of applying an external electrical field, commonly to align conductive nanoparticles in liquid-like systems such as epoxy. It has been shown that said alignment and final efficiency in forming a conductive network and as a result in enhancing electrical conductivity depends on the aspect ratio of the nanoparticles, the viscosity of the mixture and the strength and frequency of the applied electrical field [370].

In this sense, Gong and co-workers [371] studied the effects of CNT alignment on the electrical conductivity behaviour of polymer nanocomposites using a percolation network model that considers the possible distortion of adjacent nanotubes and their influence in the electrical resistance of the nanocomposites. Simulation results were in good agreement with experimental data, as shown in Figure 25, as the anisotropic electrical conduction behaviour was mainly affected by the conductive pathway density formed in each direction, dependent on CNT alignment in the matrix. As different levels of CNT alignment can be easily attained during processing and as a consequence the electrical conductivity easily adjustable, this type of system and process shows great potential in the design of multifunctional nanocomposites for applications such as smart sensing.

Figure 25

In a similar way, Endrödi et al. [373] analyzed the influence of vertically aligning MWNT arrays in the properties of conducting polymers. The particular anisotropy found in terms of the electrical conductivity of the resulting nanocomposites (50 times higher electrical conductivities were observed in the direction parallel to the nanotubes when compared to that measured perpendicularly), alongside similar thermal anisotropy, makes them ideal candidates for thermal management applications.

Khan et al. [374] reported improved electrical conductivities for epoxy-based-MWNT nanocomposites by inducing the alignment of the nanotubes as a result of dc electric fields applied during the curing process, promoting the formation of a percolative conductive network at much lower concentrations of MWNTs when compared to randomly-distributed MWNT-reinforced epoxy systems (see Figure 26). Particularly, the authors showed that it was possible to reach percolation thresholds as low as 0.0031 vol% MWNT when measuring the electrical conductivity parallel to the aligned MWNTs, more than one order of magnitude lower than nanocomposites having a random nanotube orientation (0.034 vol% MWNT) or when measuring in a direction perpendicular to MWNT orientation (transverse direction).

Figure 26

Similarly to Khan and co-workers, Ladani et al. [375] used an ac electrical current to align CNFs in an epoxy matrix and observed the formation of a chain-like CNF structure in the resulting nanocomposites (see Figure 27), leading to important increases in the electrical conductivity to as high as 10^{-2} S/m for 1.6 wt% of aligned CNFs, seven orders of magnitude higher than the conductivity of unfilled epoxy. More importantly, the alignment of CNFs allowed to significantly reduce the required CNF concentration for attaining high electrical conductivities, as the addition of increasingly higher CNF amounts reduced the conductivity increment advantage of aligning nanotubes, which the authors related to the lack of free space available for the CNFs to orient in the direction of the applied electrical field and hence higher probability of CNF aggregate formation at higher loadings (see values presented in Figure 28).

Figure 27

Figure 28

Folowing a similar procedure, Wu et al. [370] considered the alignment of GnP using an external ac electrical field with the objective of enhancing the electrical conductivity of epoxy nanocomposites. Graphene alignment resulted in nanocomposites with electrical conductivities that were 7 to 8 orders of magnitude higher than that of the unfilled epoxy (Figure 29) and significantly higher than that of nanocomposites with the same amount of randomly-oriented graphene, though differences started being less marked above 0.8 vol% GnP, which authors related to an increased difficulty in aligning GnP and higher probability of GnP aggregation.

Figure 29

3.1.7. Effect of the use of 3D carbon-based reinforcements

Besides favouring the formation of a highly electrically-conductive network throughout the polymer matrix at lower percolation thresholds by controlling nanoparticle dispersion during processing, by functionalizing/surface modifying the nanoparticles, by promoting their selective dispersion, by using nanohybrids or by promoting the alignment of said nanoparticles/nanohybrids, some researchers have recently focused their work in developing more complex 3D CNT or graphene architectures prior to their addition to polymers. In this sense, Yu and co-workers have focused their work [376-377] in establishing highly electrically-conductive networks based on carbon materials in polymer matrices by means of controlling the architecture of added CNT and/or graphene, especially when compared to the significantly lower electrical conductivities reached for polymer-based nanocomposites containing randomly dispersed carbon-based conductive nanoparticles. As EMI shielding performance is directly related to the electrical conductivity, these authors have shown the importance of forming highly electrically-conductive 3D CNT or graphene architectures prior to addition to polymer matrices in the development of novel materials for EMI shielding applications.

Particularly, Yu and co-authors [376] have considered the reinforcement of epoxy matrices by an infiltration method using a conductive framework of a previously prepared 3D CNT sponge, intended for EMI shielding purposes. Authors demonstrated the high EMI SE with only adding 0.66 wt% of 3D CNT sponge (33 dB in the X-band), higher than values commonly reached for epoxy nanocomposites containing much higher amounts (10-20 wt%) of randomly dispersed CNTs. In a similar way, Yu and co-workers [378] prepared porous graphene aerogels and effectively added these 3D graphene networks to an epoxy matrix, once again demonstrating the importance of forming a proper conductive reinforcement network prior to its addition to the matrix in reaching a nanocomposite with a high electrical conductivity and high EMI SE (in this case 35 dB) at concentrations of added aerogel as low as 0.33 wt%. In a later work [379], the authors further developed this kind of graphene-based aerogel and showed its outstanding EMI SE (around 83 dB in X-band), demonstrating their high potential to be used as functional reinforcement at extremely low amounts to create high performance EMI shielding polymer-based nanocomposites.

The same research group used other strategies for creating highly efficient electrically conductive structures prior to their addition to polymer matrices, as for instance by means of electrostatic assembling highly conductive transition metal carbide/carbonitride (MXene) into PS microspheres, followed by compression-moulding. In this way, Yu et al. [377] were able to establish a highly efficient continuous conductive network of the highly electrically conductive MXene through the PS matrix, leading to conductivities as high as 1081 S/m and to outstanding EMI SEs > 54 dB in X-band at extremely low percolation thresholds (0.26 vol% MXene).

3.2. Addition of carbon nanotubes/nanofibres

As previously mentioned, with the recent advancements in the fields of Materials Science and Nanotechnology, polymer nanocomposites have been developed as replacers of common metals for shielding electromagnetic waves, overcoming some of their limitations such as high density, poor corrosion resistance or limited electromagnetic absorption [380-381]. More recently, electrically-conductive nanocomposites based on the combination of a given polymer with conductive carbon-based nanoparticles, have been considered, especially derived from recent developments in polymer nanocomposites processing and controlled carbon-based nanoparticles syntheses, both in terms of production as well as architecture, morphology and crystalline perfection, allowing a great versatility in terms of attaining conductive nanoparticles with variable aspect ratios, geometries and chiralities [382].

It is well-known that the EMI shielding of nanocomposites depends mainly on the aspect ratio of the conductive nanoparticles, their intrinsic conductivity, dielectric constant, magnetic properties, geometry and chirality [383-385]. For that reason, two aspects have specially been considered when addressing this type of nanocomposites for EMI shielding applications: on the one hand proper nanoparticles dispersion throughout the polymer matrix and, on the other, the aspect ratio of said nanoparticles, in both cases with the objective of establishing a proper conductive network for electrical conduction and absorption-dependent EMI shielding at the lowest possible nanoparticles concentration. In the case of CNTs, given their variable structure and structure-dependent electrical properties, specific importance has been initially given to the influence of their structure, mainly chirality, on their electrical properties and hence influence on the electrical properties of the resulting carbon nanotube-based polymer nanocomposites.

3.2.1. Influence of carbon nanotube’s structure

Among CNTs, due to their particular structure and high dependence on chirality, SWNTs are the ones that have been dealt with when analyzing the influence of nanotube’s helicity on its electrical conduction behaviour and as a consequence possible influence on the electrical properties of polymer nanocomposites. Nanot et al. [386] have considered the structural, electronic, vibrational, optical, and transport, mechanical and thermal properties of SWNTs, focusing a great deal of their book chapter in the analysis of the electronic properties of this type of nanotubes, very sensitive to microscopic atomic arrangements and symmetry, as well as diameter and chirality, displaying behaviours from metallic (armchair) to semiconducting with varying band gaps (zig-zag and chiral-type). In terms of CNTs use in polymer nanocomposites, authors state that from the several possible types based on helicity, semiconducting zig-zag are particularly promising for photonic device applications, with tailor-made electrical properties based on diameter and direct electronic band gap; while metallic armchair nanotubes are considered ideal for electronic applications such as power transmission cables. Jain and co-workers [387] have reviewed the energy band structure and density of states of SWNTs of different helicities, showing the importance of structure in the electrical behaviour of the nanotubes and, as a result, in their possible efficiency in developing novel electrically-conductive polymer-CNT nanocomposites. Wang et al. [388] revealed the influence of SWNTs chirality and hence electronic properties on the thermoelectric (TE) properties of composites, showing that comparatively the addition of semiconducting SWNTs to PANI led to nanocomposite films with a maximum TE power factor that was about three times higher than that of nanocomposite films containing a similar amount of metallic SWNTs, which authors related to ultra enhanced Seebek coefficient resulting from the effective energy filtering effect at the interfaces between the semiconducting nanotubes and PANI.

Interestingly, Fujisawa and co-authors [389] demonstrated the importance of the chiralities of the inner and outer tubes in double-walled carbon nanotube (DWNT) assemblies, demonstrating the importance of the total fraction of the metallic inner and outer tubes on the conduction mechanism of DWNT samples, with the results being used to understand the conduction mechanisms of MWNTs, and supporting the development of high-performance transparent conductive films and nanofillers to be used in polymer nanocomposites [390].

3.2.2. Influence of dispersion

First of all, considering CNTs and their dispersion, Kumar et al. [391] analyzed the EMI shielding of PVDF-MWNT nanocomposites in a wide range of frequencies, from 1 GHz (L-band) to as high as 18 GHz (Ku-band). The authors showed that a simple acid treatment of MWNT prior to addition into PVDF led to nanocomposites with significantly lower percolation thresholds (0.15 wt% acid-treated MWNT compared to 0.35 wt% of untreated MWNT). Acid treatment significantly improved MWNT dispersion and interfacial adhesion with the PVDF matrix, resulting in nanocomposites with enhanced EMI shielding efficiencies. As acid treatment of MWNT enabled to significantly reduce the percolation threshold for electrical conduction, similar values of the EMI SE through the whole frequency range were attained for the nanocomposites containing acid-treated MWNTs at much lower MWNT concentrations than nanocomposites with untreated nanotubes (0.5 wt% treated-MWNTs compared to the 4 wt% of untreated MWNTs). Additionally, nanocomposites containing the acid-treated nanotubes presented an absorption-dominated EMI shielding mechanism, enabling them to be used in applications such as stealth or as radar absorbing material.

Pawar et al. [392] demonstrated that the grafting of MWNTs onto Fe_3O_4 nanoparticles could be used to enhance the EMI shielding of nanocomposites based on PC-SAN blends. Interestingly, the authors showed that by using a two step mixing process it was possible to selectively localize and guarantee proper dispersion of the conductive nanoparticles in a given polymer of the blends, particularly by solution blending the nanoparticles with PC and later melt-mixing with SAN, significantly improving the EMI shielding of the nanocomposites when compared to similar MWNT-reinforced nanocomposites. Also, it was proven that while reflection was the main mechanism of shielding in the blends with MWNTs, absorption dominated in the case of adding

MWNT-g-Fe_3O_4 nanoparticles, which could open up new possible applications for these materials for microwave absorption.

In a similar way, Kar and co-authors [393] tailored the dispersion of MWNTs in blends of PVDF-ABS with the objective of designing materials with enhanced EMI shielding. In this study the authors modified the MWNTs using an amine terminated ionic liquid that worked improving the interfacial interaction with PVDF and facilitated the formation of a MWNT network structure. Additionally, in order to pass from a reflection-dominated to an absorption-dominated EM shielding mechanism, a ferroelectric phase (barium titanate nanoparticles chemically grafted onto GO) or a ferromagnetic phase (Fe_3O_4 nanoparticles) was added to the MWNTs, a similar strategy as the one used by Pawar et al. [392]. Ferroelectric-MWNT-filled nanocomposites displayed an EMI SE that was 10 dB higher than that of the blends with only MWNTs, showing the more effective mechanism of absorption when compared to reflection.

Nayak et al. [394] used CNFs (0.25 to 5 wt%) to enhance the electrical conductivity and EMI SE of PI. The in-situ polymerization of PI in the presence of CNFs and continuous sonication during said polymerization resulted in nanocomposites with a much lower percolation threshold (0.5 wt% CNF) than reported for similar systems, which was related to improved CNF dispersion. The addition of 5 wt% CNF led to nanocomposites with an EMI SE above 12 dB in the X-band range (0.07 mm-thick film), suggesting their possible use in thin ESD and EMI shielding components.

3.2.3. Influence of the aspect ratio

In terms of the influence of the aspect ratio of nanotubes, Theilmann et al. [301] prepared nanocomposites by adding variable concentrations of MWNTs into a polydimethylsiloxane (PDMS) elastomer and demonstrated the higher EMI SE and permittivity of nanocomposites at lower loadings, for instance reaching an EMI SE of 80 dB at 5.7 vol% of MWNTs, than prior similar works found in the literature (see comparison presented in Figure 30). This improved EMI SE was related to the use of very high aspect ratio nanotubes and to an effective mixing process, which guaranteed a proper dispersion of the nanotubes throughout the PDMS matrix by a combination of pre-mixing and three-roll milling and as a result the formation of an effective conductive network, resulting in extremely low percolation thresholds (0.06 vol% of MWNT) and higher dc conductivities (1.5 S/m for 0.6 vol% MWNT and as high as 301 S/m for 5.7 vol% MWNT).

Figure 30

Verma et al. [362] analyzed the effect of the aspect ratio of MWNTs on the EMI shielding in the X-band range of MWNT-reinforced ethylene-propylene random copolymer nanocomposites prepared by melt-mixing in a twin-screw extruder with melt recirculation. Two types of MWNTs having very different aspect ratios, long length MWNTs (l-MWNT) with a diameter of 10-100 nm and length of 35-50 μm (high aspect ratio: 1356-1937), and short length MWNTs (s-MWNT) with a diameter of around 9.5 nm and an approximate length of 1.5 μm (lower aspect ratio: ≈ 158), were considered. Melt recirculation during processing was proven to guarantee a proper dispersion of the MWNTs, as nanocomposites presented low percolation thresholds (0.45 and 1.07 wt%, respectively for l-MWNT and s-MWNT-reinforced nanocomposites). Interestingly, direct consequence of the higher absolute electrical conductivity and highly-disordered structure of l-MWNT within the polymer matrix, l-MWNT-reinforced nanocomposites presented better shielding at lower nanotube concentrations (up to 4 wt%) than s-MWNT-reinforced nanocomposites, which displayed better attenuation behaviour at higher MWNT loadings (compare Figure 17(c) with Figure 17(f)).

Al-Saleh [395] analyzed the influence of the formation of an effective conductive percolation network on the EMI shielding of MWNT-polymer nanocomposites in the X-band frequency range, comparing the experimental results of MWNT-reinforced UHMWPE nanocomposites prepared by placing the CNTs at the external surface of UHMWPE powder by wet mixing with other results found in the literature for similar systems (see Table 1). As expected, EMI SE was found to increase with increasing the amount of MWNTs, with an EMI SE as high as 50 dB being reported for a 1 mm thick plate by adding 10 wt% of MWNTs. The particular nanocomposite structure resulting from wet mixing was found to significantly reduce the percolation threshold (reaching values as low as 0.054 vol% MWNT) and hence enhance EMI shielding by absorption (thicker MWNT layer) and reduce the contribution due to reflection (decrease in the external surface area of the conductive network), reaching values as high or even higher than obtained for MWNT-reinforced polymer nanocomposites prepared by melt-mixing, solution blending or a combination of both having a fine and well-dispersed MWNT microstructure [396-400]. So, interestingly, the author was able to demonstrate that the distribution of the conductive MWNTs and thickness of the conductive network play a crucial role and may be tuned in order to enhance the EMI SE of nanocomposites by promoting the absorption loss factor. The thicker the MWNT layer the higher the absorption and as a result the lower the re-reflected EM waves (see scheme of EM wave interaction with a shielding material presented in Figure 15).

Jia et al. [401] demonstrated that it is possible to some extent to devise specific CNT networks in order to regulate the EMI SE of MWNT-reinforced PE nanocomposites. Particularly, the authors prepared nanocomposites having three different conductive networks (see Figure 31): a nanocomposite having a segregated MWNT structure (s-CNT/PE), prepared by mechanical blending the nanotubes with previously crosslinked PE granules and later applying hot compaction; a partially-segregated MWNT nanocomposite (p-CNT/PE), prepared by mechanical blending the nanotubes with non-crosslinked PE granules and later applying hot compaction; and a third nanocomposite with a randomly-distributed MWNT structure (r-CNT/PE), prepared by mixing the PE granules and nanotubes using solution blending and later applying hot compaction. Comparatively, the s-CNT/PE nanocomposites exhibited lower percolation thresholds and electrical conductivities that were up to two orders of magnitude higher than those of p-CNT/PE and r-CNT/PE nanocomposites at the same MWNT concentration, related to an increase in the effective CNTs that participate in the pathways of the conductive network. As a consequence, s-CNT/PE nanocomposites showed higher EMI shielding efficiencies, reaching values as high as 46.4 dB for a 5 wt% MWNT loading, in this case related to the higher efficiency of the MWNT segregated structure (higher number of CNT interfaces) to absorb the EM waves (absorption-dominated shielding mechanism, highly effective at the high frequencies of the X-band range) (see Figure 32).

Figure 31

Figure 32

Bera et al. [351] considered the preparation of electrically-conductive PCL-MWNT nanocomposites through solution blending of PCL and MWNTs in the presence of PCL beads, selectively dispersing the nanotubes in the solution blended region and guaranteeing the formation of an MWNT interconnected conductive network (see scheme of nanocomposite preparation shown in Figure 33). As a result, electrical conductivity (approximately 2.5×10^{-2} S/cm for 0.15 wt% MWNT) and EMI SE in the X-band frequency range (around 24 dB at 1.8 wt% MWNT), in both cases in the presence of 70 wt% PCL beads, were significantly increased at very low MWNT concentration. The addition of the PCL beads acted concentrating the MWNTs in the solvent dried PCL phase, helping to create a more effective conductive MWNT network throughout the matrix. Hence, the addition of increasingly higher concentrations of PCL beads helped to further increase the electrical conductivity and EMI SE even at low MWNT loads (see EMI SE values presented in Figure 34).

Figure 33

Figure 34

Mohanty et al. [402] studied the EMI SE of MWNT-reinforced PES and PEI nanocomposites prepared by mixing variable concentrations of MWNTs (from 0.5 wt% to 5 wt%) using solution blending. Authors showed that the EMI SE measured in the X-band range increased with frequency and MWNT concentration, with no significant differences between polymer matrices. Comparatively, both PES and PEI nanocomposites containing 5 wt% MWNT exhibited shielding efficiencies at 8 GHz between 42 and 45 dB, clearly above the values of pure polymers (1-2 dB), with a gradual shift from reflection to absorption as main shielding mechanism being observed at higher frequencies with increasing MWNT concentration, once again attributed to an increase in the dielectric loss values.

3.3. Addition of graphene and graphene-based materials

Besides CNTs and CNFs, graphene and graphene-based materials have recently been considered as interesting possibilities to enhance the electrical conductivity and EMI SE of polymers.

3.3.1. Influence of dispersion

Mohan et al. [403] designed PAN-graphene films for broadband EMI shielding applications, the resulting nanocomposite films displaying shielding efficiencies of around 42 and 32 dB, respectively in the C-band (4-8 GHz) and X-band frequency ranges, in both cases corresponding to more than 99.99% microwave attenuation. Nevertheless, shielding was mainly reflection-dominated, which could open even further enhancements through finding the way to shift it to a more absorption-dependent shielding mechanism.

Panwar et al. [404] studied the dielectric properties of PP-graphite composites prepared by melt-mixing and hot compaction in low and radio frequency ranges, as well as the EMI SE in the radio frequency range. Above the percolation threshold the prepared composites presented high values of ac conductivity and exhibited almost no frequency dependence, both at low as well as high frequencies, hence constituting good possibilities for EMI shielding, though the main contribution to shielding was still reflection. A maximum value around 44 dB was obtained at 2.76 GHz for composites containing an amount of graphite of 0.075 vol%, which, together with the high dielectric constant and dissipation factor, would enable the use of these materials in charge storing devices or EMI shielding components.

Yao et al. [405] proved that graphene could be more properly dispersed in a PVC matrix with the help of ferromagnetic Fe_3O_4 nanoparticles, which, not only helped improve the fire retardancy of nanocomposites through the formation of a network-like structure due to the good dispersion of graphene, but specially enhanced the electrical and magnetic properties of the nanocomposites, showing high EMI SE in the X-band range (13 dB). Still, as reflection mechanism dominated, EMI SE was a bit low when compared to similar graphene-based systems (see values presented in Table 2), a problem that could be partially solved by optimizing the proportion between graphene and Fe_3O_4 nanoparticles.

In a similar way as other authors that used MWNTs, Gupta et al. [411] modified the surface of graphene in order to develop novel materials with improved absorption-dominated EMI shielding efficiencies. Particularly, they considered multilayer graphene anchored with titanium dioxide (TiO_2) combined with already conductive polypyrrole (PPY). By varying the amounts and proportions of graphene and TiO_2, authors were able to reach a maximum total SE of 53 dB in the high frequency range 12.4-18 GHz (Ku band), the nanocomposite coming as a good alternative for EMI shielding applications, specially those that are absorption-dominated.

3.3.2. Influence of the use of nanohybrids

Other hybrid fillers based on graphene or graphene-based materials have also been considered as possible strategy to enhance the EMI SE of polymers. Such is the case of silver decorated rGO, as shown by He and Tjong [412], which considered the addition of said nanohybrids to PVDF and preparation of nanocomposites by solution blending. A low percolation threshold was attained (0.17 vol%), as the hybrid nanofillers were homogeneously dispersed throughout the polymer matrix, with the nanocomposites displaying electrical conductivities that resulted one order of magnitude higher than that of similar PVDF nanocomposites containing thermally-reduced graphene, related to the high intrinsic electrical conductivity of silver. This global enhancement of electrical conductivity could enable the use of these novel nanocomposites for EMI or RFI shielding applications.

Similarly, Mural et al. [413] used nickel nanoparticles to decorate GO in order to create nanohybrids to be used as EMI shielding enhancers in polymers. The authors added the nanohybrids and, as Pawar et al. with MWNTs [392], were able to selectively localize them in a specific phase of PE-PEO polymer blends, reaching values of EMI SE as high as 70 dB for a 6 mm thick shield at a frequency of 17.1 GHz, which were partially related to the simultaneous reduction of GO while synthesizing GO-Ni nanohybrids. Also, the combination of GO-Ni nanohybrids with conductive MWNTs and later addition to the blends led to nanocomposites with enhanced absorption-dominated EMI SE.

Shahzad and co-workers [414] considered a method to enhance the EMI SE of rGO-PS nanocomposites that consisted of doping the rGO with sulphur, particularly sulphur having a thiophene-like structure by simply heating a mixture of GO and sulphur powder. Direct consequence of the much higher electrical conductivity of the sulphur-doped rGO than undoped rGO, nanocomposites containing the doped nanoparticles presented much higher electrical conductivities than nanocomposites with undoped rGO (150% higher) and, as a result, improved EMI SE (24.5 dB, compared to the 21.4 dB of undoped rGO-PS nanocomposites, in both cases by adding a concentration of 7.5 vol% of nanoparticles).

As the synergistic effect of magnetic loss and dielectric loss greatly contributes to the improvement of EMI SE [415-420], it is necessary to review the most recent advances on polymer nanocomposites containing carbon-based materials (dielectric components) and magnetic nanoparticles, thought to enhance the microwave penetration and absorption of dielectric components [421]. In this sense, Yu et al. [422] showed the effect of adding magnetic Fe_3O_4 nanoparticles to PS/graphene composites in enhancing their EMI SE. Fe_3O_4-RGO and Fe_3O_4-TGO hybrids were prepared and added to PS by solution blending, the addition of Fe_3O_4-TGO leading to much higher electrical conductivity and EMI SE values (> 30 dB, 9.8-12 GHz range at 2.24% of Fe_3O_4-TGO) due to enhanced dispersion throughout the PS matrix. In a similar way, the incorporation of combined carbonyl iron (CI) and TGO sheets to epoxy led to nanocomposites with higher magnetic losses, which, combined with their higher electrical conductivity, resulted in materials with improved EMI shielding characteristics [423]. Comparatively, the addition of combined CI and TGO resulted in EMI SEs that were much higher than that of epoxy nanocomposites with the same amount of only TGO (> 36 dB compared to around 20 dB), the use of magnetic CI resulting in wave absorption loss as the main EMI shielding mechanism.

Other authors have considered the combination of CNTs and graphene-based materials to enhance the EMI SE of polymers. Recently, Singh and co-workers [424] have considered not only the combination of both types of conductive carbon-based nanoparticles having different morphologies, in their case tubular-like CNTs and layered rGO, but also the influence of vertically aligning the nanotubes, modifying them with magnetic Fe_3O_4 nanoparticles and sandwiching them between rGO layers (see Figure 35), reaching shielding efficiencies higher than 37 dB in the Ku-band, above the minimum value of around 30 dB recommended for many high frequency EMI shielding applications.

Figure 35

Maiti and Khatua [425] optimized the ratio of GnP and MWNTs added to a PC matrix and combined it with a high temperature of melt-mixing for preparing the nanocomposites in order to reduce the melt viscosity of PC and favour nanoparticles dispersion, and were able to reach a high EMI SE of around 21.6 dB at a relatively low concentration of conductive nanofillers (4 wt%), higher than that reached when individually using only graphene or only CNTs.

3.4. Post-processing of carbon-based polymer nanocomposites for EMI shielding

Advances in carbon-based polymer nanocomposites for applications requiring electrical conduction and for EMI shielding applications need to consider recently used post-processing techniques, namely due to their high interest and versatility three-dimensional (3D) printing and electrospinning.

3.4.1. Three-dimensional printing

From all post-processing techniques that have considered the use of polymer nanocomposites containing carbon-based nanoparticles for EMI shielding applications, including more common transformation processes such as injection-moulding, compression-moulding or solvent casting, 3D printing is the one that has gained more interest from both academia and industry in recent years, mainly due to the great deal of development of this technique, both in terms of hardware as well as in the study of novel multifunctional materials adapted to 3D printing, as well as its capability for fabricating complex shapes at moderate speeds without mould requirement. Although fused deposition modelling (FDM) has been the most frequently used 3D printing method, other techniques such as selective laser sintering (SLS) [426], micro-stereolithography (MSL) [427-428], UV-assisted 3DP (UV3DP) and solvent cast 3DP (SC3DP), have also been used.

Recent reviews have considered 3D printing as post-processing technique to develop novel multifunctional components from carbon-based polymer nanocomposites [429-430], focusing on the different available techniques and their characteristic features (advantages and limitations), the importance in the preparation of the nanocomposites for 3D printing, resulting multifunctional properties, especially in terms of electrical conductivity and EMI shielding, potential applications and future scopes. Based on final characteristics and especially high resulting electrical conductivity, the most widespread use of 3D-printed carbon-based polymer nanocomposites is in electronics, including energy storage devices, electronic components such as transducers, flexible conductors, emitters, radio frequency inductors, EM wave absorbers, liquid sensors, and electrical micro-interconnectors. Other interesting possibilities include 3D printable biomaterials electrical stimuli to enhance cell functions for tissue engineering [429].

In terms of market, Ghoshal states in his review [429] that it is predicted that by 2019 the 3D-printing market could reach 10 billion dollars, with an average annual growth rate of 32.2% from 2014 to 2019, with an expected importance being given to the development of multifunctional materials, especially carbon-based polymer nanocomposites [431-432].

Chizari et al. [433] have recently developed highly conductive polymer nanocomposites based on CNTs and PLA and used them as the ink for SC3DP (see Figure 36(a)), a technique characterized by its relatively low cost and the rather easy possibility of adjusting the viscosity of the ink by modifying the amount of used solvent, hence enabling to print nanocomposites with high nanofiller content. Interestingly, after developing PLA-CNT inks with outstanding electrical conductivities reaching 5000 S/m, SC3DP of PLA-CNT scaffolds led to significant improvements of the specific EMI SE when compared to equivalent nanocomposites prepared by hot-pressing (around 70 $dB \cdot cm^3/g$ compared to around 37 $dB \cdot cm^3/g$), at the same time controlling the transparency of the scaffold by modifying printing patterns and inter-filament spacing, hence coming as good alternative for EMI shielding applications where transparency may result advantageous, as in aerospace systems or in portable electronic parts (see scaffolds with different printing patterns showing their transparency in Figure 36(b)) .

Figure 36

Prior to Chazari et al. [433], Guo and co-workers [434] had already developed PLA-CNT nanocomposites, finding an electrical percolation threshold around 0.3 wt% CNT, and prepared highly efficient helical liquid sensors using the SC3DP technique.

Gnanasekaran et al. [435] used the FDM technique to print electrically-conductive CNT- and GnP-based PBT nanocomposites. Comparatively, printing of PBC-CNT led to parts with higher electrical conductivity at much lower nanofiller concentration than PBT-GnP (0.49 wt% CNT vs 5.2 wt% GnP in terms of electrical percolation threshold and around 20 S/m vs 2 S/m in terms of electrical conductivity for maximum amount of CNT and GnP, respectively). Authors explained this big percolation threshold difference between CNT and GnP based on the dimensionality of the nanofiller particles (1D for CNT and 2D for GnP) and higher GnP aggregation, increasing electrical resistance. Interestingly, authors demonstrated that in order to attain a uniform electrical connectivity between FDM's deposition lines it is advisable to add nanofiller contents clearly above the percolation threshold.

Schmitz and co-workers [436] used FDM to manufacture components based on more common ABS considering the addition of variable amounts of CNTs, CB and a 50/50 CNT/CB nanohybrid. For this purpose, said nanofillers were previously melt-mixed with ABS using an internal mixer, with preliminary rheological results indicating optimum 3 wt% nanofiller for filament production for 3D printing. Although highly dependent on 3D printing patterns, all nanocomposite 3D-printed components presented higher electrical conductivities and higher EMI SEs than neat ABS, with ABS/CNT showing the highest values (maximum EMI SE around 16 dB), followed by

ABS/CNT/CB and finally by ABS/CB nanocomposite. In all cases, authors demonstrated that the commanding mechanism of shielding was absorption.

Kim and co-authors [437] have considered the use of FDM to print PVDF-based nanocomposite films combining piezo-, pyro- and di-electric $BaTiO_3$ with electrically-conductive CNT, used to increase dielectric constant and guarantee a more uniform dispersion of $BaTiO_3$ nanoparticles. As CNT electrical percolation was found at 1.7 wt%, the most desirable combination of dielectric constant and loss properties (118 and 0.11 at 1 kHz, respectively) was achieved at said concentration of nanotubes and at 45 wt% $BaTiO_3$, higher than equivalent solvent-cast PVDF films, as 3D printing limited defect formation and facilitated molecular dipole alignment. Although the study mentions that significant efforts are still required to reduce the dielectric loss by means of enhancing the dispersion of nanoparticles, including surface modification, it demonstrates the feasibility to integrate 3D printing to the production of dielectric devices with almost freedom of design to be used in electronics or in energy storage applications.

Researchers have set the following critical parameters for obtaining 3D-printed components with high EMI SEs based on carbon-based polymer nanocomposites: first of all, the need to prepare 3D-printable filaments with an electrical conductivity as high as possible, which, as already seen in previous sections, will depend on nanofiller selection, concentration and dispersion; secondly, the limitation of some printing techniques in processing highly viscous nanocomposites (nanoparticle addition tends to enhance the global viscosity of the material), leading to non-uniform printing due to flux instability and even printing nozzle blockage, especially for methods like FDM [438]; and third, a careful control of the printing pattern, in order to diminish as much as possible the electrical resistance to the movement of charges, normally related in 3D-printing components to lacunas, microvoids, low material compaction or structural anisotropy. In the case of polymer nanocomposites, it has to be stated that preferential and selective localization and alignment of the nanoparticles may be possible by carefully controlling printing direction (see Figure 37).

Figure 37

3.4.2. Electrospinning

Besides 3D-printing, electrospinning has arisen in the last years as an interesting post-processing technique to prepare novel multifunctional carbon-based polymer nanofibres, particularly thought when high electrical conductivity and high EMI SE are required for a given component. Besides versatile and cost-effective, when compared with other processing techniques electrospinning allows under specific conditions to properly disperse carbon-based nanoparticles throughout a polymer matrix with nanofibrous structure on a quite large scale [439-441]. Given the particular final nanofibre/nanowire-like structure, electrospinning has been used to fabricate supercapacitors or Li-ion batteries, among other applications [442-445]. Nevertheless, only recently this technique has been considered to develop novel nanofibrous components with high electrical conductivities and EMI absorption characteristics based on carbon-based polymer nanocomposites.

The research group of Nasouri has dedicated a lot of work to the design, modelling and manufacturing of electrospun carbon-based polymer nanofibres, especially using carbon nanotubes, specifically thought for EMI shielding applications and as microwave absorbing materials. In this sense, Nasouri and co-authors developed PVA-CNT nanofibres containing variable concentrations of nanotubes using electrospinning with the aim of using them as EMI shielding material (typical surface morphology of PVA-CNT electrospun nanofibres is presented in Figure 38 for different CNT concentrations) [446-448]. Interestingly, authors demonstrated that that for a CNT content of 7.7 wt% the final electrospun nanofibres displayed a high electrical conductivity and an absorption-dominated EMI shielding mechanism, with an approximate high EMI SE around 31.5 dB due to absorption and only around 8.8 dB due to reflection. The same authors had previously compared the experimental electrical conductivity and EMI SE values of PVP-CNT electrospun nanofibres [447], finding an electrical percolation threshold of around 1 wt% CNT and an absorption-dominated EMI SE up to 42 dB (obtained at 10 wt% CNT), with those calculated from theoretical models, showing that the theoretical prediction agreed well with the experimental values obtained for the electrospun nanofibres containing the highest amounts of CNT (7.5 and 10 wt%).

Interestingly, Wang and co-workers [449] have recently considered the already mentioned strategy of combining carbon-based nanoparticles, in this case graphene, with micrometric-sized particles, more specifically SiC nanowires, to tune the EM absorption shielding of developed electrospun nanofibres. The hybrid nanowires consisting of SiC encapsulated with graphene displayed enhanced EM shielding performance due to the dielectric loss resulting from graphene and SiC defects, interfaces between both materials, and dangling bond of nanowires surface, coming as excellent combined reinforcements and EMI SE enhancers form polymers.

Figure 38

As has been seen, one of the current trends in polymer nanocomposites for electrical and EMI shielding applications lies in guaranteeing on the one hand a proper dispersion of the conductive nanofillers and formation of an effective conductive network, which can be attained using different strategies, such as enhanced mixing, addition of higher aspect ratio nanofillers or the use of nanohybrids, and, on the other, an absorption-dominated EMI shielding mechanism. Although this has been reached in some polymer nanocomposites, as already shown in this section, the next section will focus on one of the most promising and already proven strategies: carbon-based nanocomposite foams.

4. Carbon-based cellular nanocomposites for EMI shielding

4.1. Preparation techniques

Current industrial trends have focused on the development of more efficient materials in order to reduce manufacturing costs and save energy. In this sense, lightweight materials with improved specific mechanical properties and functionalities are attracting considerable attention, with polymer foams appearing as promising candidates with possibility of customization for specific purposes by controlling their composition [450]. With only slight variations, foaming processes used to prepare polymer nanocomposite foams based on polymers with nano-sized carbon-based particles are basically the same as the ones industrially available for producing polymeric foams [5]. Mentioned foams have received an increasing attention at scientific and industrial level in comparison with metal-based EMI shielding material due to their reduced density, high chemical stability and low-cost [451].

Utilizing foaming agents is the most common technique to generate a controlled cellular structure in thermoplastic polymers. Depending on the application and polymer, various techniques are used to introduce the physical or chemical blowing agent in the liquid/melt state by extrusion, injection-moulding or compression-moulding, or in the solid state where gas is forced into a solid polymer followed by depressurization or heating to release the dissolved gas [452]. Said foaming techniques can be applied using both discontinuous processes such as batch foaming and injection-moulding, as well as continuous processes such as extrusion. Additionally, other foaming methods such as phase separation [26, 453] and leaching [454] have been used to prepare porous materials with carbon-based nanoparticles at the laboratory scale for specific purposes.

4.2. Morphology and cellular structure

Controlling the foaming process variables, the morphology and cellular structure of foams can be tailored to serve in a specific application. The foaming process can also modify the dispersion and orientation of the carbon-based fillers, causing network assembly or exfoliation of the stacks. In batch foaming process the saturation of the material with foaming agent can be carried out either below or above the glass transition temperature (T_g) of the polymer. If the dissolving temperature is higher than the glass transition temperature of the polymer, the release of pressure would result in supersaturation and cell nucleation and growth. Cell structure is usually fixed by cooling the materials below their T_g [452]. When the saturation temperature is lower than the T_g the cells are not able to nucleate and grow after the release of pressure even if gas is in the supersaturation state due to the glassy nature of the polymer and foaming could occur when temperature is raised above the T_g and the cellular structure is again fixed by cooling the material [452]. The major variables that control the cellular structure are the saturation temperature, pressure, and pressure drop rate, and, in the second case, the temperature ramp rate.

Gedler et al. [455-456] prepared PC/graphene nanocomposite foams with a closed-cell structure via 1 and 2 step batch foaming using supercritical carbon dioxide and found out that the 1-step foaming method led to improved dispersion and distribution of GnP where the dispersion/exfoliation is believed to be the result of strong attractive interaction of CO_2 molecules and the graphitic structure. In both studies, the cellular structure features of foamed nanocomposites were found to depend on the presence of graphene, amount of dissolved supercritical CO_2, and CO_2 saturation/foaming conditions. TEM micrographs of prepared samples using 1-step foaming method showed that foaming led to improved dispersion and distribution of GnP. As can be seen in Figure 39, foaming via 2-step process also resulted in partial exfoliation of the graphene nanoplatelets when compared to the unfoamed material.

Figure 39

Antunes et al. [457] also showed that in the case of CO_2 dissolution foams with graphene, there was an important increment of the relative intensity between the characteristic (002) graphene diffraction peak for the solid and that of the foam, and most importantly the disappearance of this peak for some of the more expanded foams, revealing an important exfoliation of GnP due to foaming. On the contrary, graphene-reinforced chemical foams presented a much smoother increment of the relative intensity of the (002) peak, presenting a lower exfoliation of GnP due to lower foam expansion. A similar trend was observed for the CNF-reinforced foams in terms of the characteristic CNF (002) crystal plane. Although this peak still appeared in the foams, there was an important reduction with foaming, with the higher expanded CO_2 dissolution foams leading to higher relative intensity increments than the less expanded chemical foams, demonstrating that supercritical CO_2 dissolution foaming promoted the separation of the nanofibres.

Similar results have been found when using a chemical blowing agent based on PVC/MWNTs, where the cell size and distribution of closed-cell structure were affected by the chemical foaming agent and CNTs' concentration [458]. It was also demonstrated that when functionalized MWNTs are employed, the nanocomposite foams display higher cell densities and smaller cell sizes than those of samples containing non-functionalized MWNTs. Preparation of other polymeric foams such as PMMA [459-460], ethylene propylene diene monomer rubber [461], PVDF [462], PU [463-465], among many others, have been carried out for better understanding the EMI shielding efficiency of polymer foams containing conductive carbon-based nanofillers.

4.3. EMI shielding behaviour

Significant improvements can be achieved through foaming of polymers in terms of EMI shielding applications. First of all, the weight of the materials can be considerably reduced, which is essential in some applications such as aircraft and telecommunication technologies. Secondly, although the filler is diluted in total volume, the concentration of particles within the cell walls of the foams keeps the average distance between them almost the same, which is highly desirable when high electrical conductivity is required at low carbon nanofiller loading. Finally, the presence of air inside the materials decreases the real part of the permittivity, consequently reducing the reflectivity at the nanocomposite's surface [383, 466]. As expected based on the inherently high transport properties of carbon-based nanoparticles, their incorporation into foams has been vastly used as a possible strategy to enhance the intrinsically low electrical conductivity of polymer foams. Among the mentioned carbon-based nanoparticles, MWNTs have been the most common nanoparticle reinforcement in polymer foams, though CNFs have also found various industrial applications due to their lower cost. Graphene-based materials have been more popular among scientific works recently, due to some properties derived from their platelet-like geometry.

Table 3 presents a selection of recent works on polymer foams with EMI shielding ability and their electrical conductivity properties, taking into account the type of polymer, the foaming process, optimum nanofiller content and the EMI shielding efficiency and electrical conductivity of the resulting nanocomposites, as well as the main shielding mechanism. Multiple studies mentioned in this section claim that polymer foaming provides a great advantage in EMI SE with lightweight efficiency.

As, besides the absolute value of electrical conductivity, the EMI SE of a nanocomposite depends on its thickness after processing [475-476], foaming may come as a straightforward strategy to easily increase the thickness by introducing a controlled cellular structure and, if electrical conductivity is not greatly reduced, improve the overall EMI SE [477-478]. Yu and co-workers have proven the viability of this strategy by foaming MXene-based nanocomposites and reaching EMI SEs of around 70 dB, considerably higher than the already high EMI SE values of the unfoamed film counterpart (53 dB), as thickness increase and controlled porous structure led to highly efficient electromagnetic wave attenuation, facilitating a higher absorption attenuation when compared to the unfoamed film counterpart by providing a higher number of interfaces for multiple wave reflection and scattering (combination of absorption and multiple reflection mechanisms [478-480] – for further explanation consult section "2.2. Electromagnetic interference shielding efficiency (EMI SE)"). Besides the large surface areas attained in porous/foamed materials, enhancing EMI shielding by promoting multiple reflection, the high interfacial areas between carbon-based nanoparticles and polymer matrices also contribute to multiple wave reflection, hence the combination of the two strategies ultimately resulting in materials with extremely high EMI SEs [476]. Previous works have shown that the multiple reflection contribution to the EMI shielding starts to be significant when the shielding efficiency due to absorption is less than around 15 dB [459, 481-482].

Among high performance polymers, PEI has been the case of study for electrical conductivity and electromagnetic shielding. Ling et al. [453] reported a facile approach to produce lightweight microcellular PEI/graphene nanocomposite foams with a density of about 0.3 g/cm^3 by a phase separation process in which the in-situ generated extensional flow induced the re-dispersion and orientation of GnP located on the cell walls, decreasing the electrical percolation concentration and increasing the specific EMI shielding efficiency (36.1 dB·cm^3/g for 7 wt% graphene and 44.1 dB·cm^3/g for 10 wt% graphene, respectively 2.2 and 2.5 times higher than the specific EMI SEs of the unfoamed counterparts). The authors demonstrated that the generation of a microcellular structure further increased the contribution of EM absorption in detriment of reflection, shielding due to wave absorption reaching in some cases almost a 99% of the total shielding efficiency.

Yang and co-workers [471] used a simple solvent evaporation induced phase separation to prepare microcellular PI foams containing a combination of rGO and MWNTs, quantitatively demonstrating the synergistic effect of both nanofillers in enhancing both the electrical conductivity as well as EMI SE of microcellular PI foams (respectively reaching values of 1.87 S/m and 16.6-18.2 dB for a total nanofiller content of 8 wt%), the dominating EMI shielding mechanism being absorption.

Shen et al. [483] proposed a theory of multiple reflection as the absorbing mechanism, which mainly results from the reflection at multiple interfaces or surfaces of conducting fillers in the foam. As illustrated in Figure 40(a), the microcells in the PEI/graphene-Fe_3O_4 foams provided a large cell-matrix interface area. The incident electromagnetic waves entering the composite foam could be repeatedly reflected and scattered between these interfaces, hindering their escape from the composite foam until being dissipated as heat. In addition, the layered structure and high aspect ratio of the filler can cause multiple reflections, as demonstrated in Figure 40(b) and (c).

Figure 40

Similarly, Alkuh et al. [460] and Zhang et al. [484] showed that the respective addition of MWNTs and Fe_3O_4-MWNTs hybrids to PMMA and control of the resulting cellular structure after foaming by means of supercritical CO_2 led to significant increases in the specific electromagnetic absorption mechanism with increasing cell density and reducing cell size, related to the previously mentioned enhancement of the multiple reflection mechanism. For example, PMMA foams with 7 wt% of Fe_3O_4-MWNTs hybrids displayed an EMI SE of 50 dB·cm^3/g over the X-band, extending their possible application in the electronics and aerospace sectors.

Furthermore, PS foams filled with CNFs and CNTs were studied by Yang et al. [485-486] in terms of their EMI shielding response, with the foamed nanocomposites presenting a specific EMI SE of 23 dB·cm^3/g over that of copper metal sheets at 8-12

GHz (33 vs. 10 dB·cm^3/g). An EMI SE of 20 dB resulted at much lower nanofiller concentrations with CNTs in comparison with carbon fibres, owing to their higher aspect ratio (7 wt% vs. 20 wt% at 8-12 GHz). However, the reflectivity of the CNTs foams was only slightly reduced compared to that of unfoamed samples and maintained the main shielding mechanism, probably due to a too high CNT fraction (7 wt%).

Gedler et al. [455-456] showed that the EMI shielding properties of PC/graphene nanocomposite foams could be improved with increasing cell size, which promoted isotropic/random orientation of graphene particles, in this case reflection being the dominant EMI shielding mechanism. EMI shielding efficiency values were slightly higher in PC/graphene foams prepared by 1-step batch foaming than that of foams with considerably lower relative density prepared by the 2-step method due to larger cell size. Previous studies state that increasing the filler content will be followed by an increase of both reflection and absorption-based EMI shielding at low concentration levels, whereas at high conductive filler concentrations the reflection properties would be weakened maintaining a high absorption contribution [487]. Gedler et al. also investigated the electrical conductivity of the foam claiming that the composite foam conductivity did not improve drastically compared to neat PC and unfoamed PC with 0.5 wt% of graphene content and the crystallinity did not seem to affect this property of the nanocomposite foam.

A similar study about PCL/CNTs nanocomposites foamed by supercritical CO_2 batch foaming [320] revealed a very high shielding effectiveness at very low CNT content (60 dB at 0.249 vol% and 20 dB at 0.107 vol% for a material thickness of 2 cm). Said improvement of shielding efficiency response was assumed to be an effect of excellent CNTs dispersion and of the improvement of the electrical conductivity upon foaming as exemplified by a foam containing 0.107 vol% MWNTs that showed the same electrical conductivity value as an unfoamed sample with 0.16 vol% MWNTs. Additionally, a foam with 0.249 vol% of MWNTs presented a conductivity that was double the value of an unfoamed nanocomposite filled with 0.48 vol% of MWNTs.

Several authors have recently considered the use of biodegradable polymers in order to solve non-degradation issues of lightweight conductive polymer composites as alternatives to metal-based EMI shielding materials. In this direction, Kuang and co-workers [473] considered the combination of biodegradable PLLA and MWNTs and later foaming by sc-CO_2 foaming and were able to prepare highly electrically conductive foams with an EMI SE as high as 77 dB·cm^3/g with a lower electromagnetic wave reflection in the X-band frequency region.

The group of Park [474] has developed porous PLA/MWNT nanocomposites with extremely high EMI SEs by promoting the formation of a segregated conductive MWNT network by coating previously expanded PLA beads with MWNTs and later sintering the coated beads using hot-steam (see Figure 41). The combination of extremely low density, together with the developed microcellular structure of expanded PLA beads, and high electrical conductivity at extremely low MWCNT percolation thresholds resulting from the formation of a 3D MWCNT continuous conductive network throughout the material, promoted an absorption-dominated shielding mechanism and induced a high EMI SE (up to 45 dB) and outstanding specific EMI SE (as high as 1010 dB·cm^3/g), superior than any other shielding material reported so far, including common metals or conductive polymer composites and their foams. This work demonstrates how once EM waves enter a microporous PLA bead they are scattered or multi-absorbed by the formed cell walls and especially by the electrically-conductive MWCNTs (see illustration presented in Figure 42), endowing the foams with superior EMI SEs than similar materials.

Figure 41

Figure 42

Polypropylene foams containing CNTs have also been attracting scientific attention for both electrical and EMI shielding efficiency studies. A study carried out on PP/CNT nanocomposite foams by Tran et al. [470] illustrates the electrical and EMI performance of samples containing 0.05 to 0.184 vol% CNTs in foamed material with volume expansions of approximately 28. The obtained results indicate that the pore size decreased with increasing CNTs' content due to change of temperature and pressure window for different amounts of CNTs in PP. Larger pore size and lower cell density resulted in a reduction in the shielding efficiency and absorption of samples with slightly lower CNT content due to a downfall in conductivity. The sample with 0.184 vol% acted as both shielding and absorptive material with highest shielding efficiency among other samples. Contrarily to the mentioned work, where the electrical conductivity was discussed using a percolation model, Antunes et al. [488] discussed the electrical conductivity of PP/CNF nanocomposite foams where the conductivity was only slightly increased for contents higher than the critical concentration, appropriate assuming a tunnel-like conduction model. It was also mentioned that comparing the electrical response from a tunnel conduction point of view foams presented a random-distributed fibre-like system behavior, while solids presented a behavior similar to that of random-distributed spherical particles, indicating that the foaming process globally reduced CNF aggregation and brought fibres closer together.

Ameli and co-workers [489-490] have studied the electrical properties and EMI SEs of PP foams containing carbon-based fillers, from more common micrometric-sized carbon fibres (CF) [490] to nanosized carbon nanotubes [489]. In the case of the first, PP-CF foams were prepared by injection-moulding using pressurized N_2. Authors demonstrated that cell growth resulting from foaming promoted fibre interconnectivity and changed fibre orientation in the final injection-moulded parts, reducing the electrical percolation threshold from 8.5 to 7.0 vol% CF, enhancing the through-plane conductivity up to six orders of magnitude and the specific EMI SE up to 65% (> 20 dB in terms of EMI SE). Although the dominant EM attenuation mechanism for both unfoamed and foamed parts was absorption (around 80% for 10 vol% CF), increasing continuously with augmenting CF's content, comparatively PP-CF foams presented a higher contribution to EMI SE from absorption when compared to the unfoamed counterparts, globally resulting in higher total EMI SEs for the foams. The improved EMI SE due to absorption in the foams was explained by the authors based on the combination of change of fibre orientation during foaming and increased CF interconnectivity (enhanced electrical conductivity and permittivity), and enhanced wave scattering due to the cellular structure (see Figure 40). The same research group further extended their work to PP nanocomposite foams containing variable amounts of MWNTs [489]. The addition of said nanotubes, besides the generation of a uniform nanocellular/microcellular structure through foaming, led to outstanding percolation threshold decreases from 0.5 vol% MWNT (unfoamed specimens) to as low as 0.09 vol% MWNT (foams), and respective electrical conductivity increases up to two orders of magnitude, which authors once again related to the redistribution and interconnection of MWNTs through biaxial stretching during foaming.

Although rarely reported when compared to thermoplastic-based nanocomposites, thermosetting polymer nanocomposite foams, especially epoxy-based, have recently generated interest for the design of EMI shielding materials due to epoxy's good adhesion to substrates, good chemical and heat resistances, low shrinkage during processing, among other features. The main problem of these materials for EMI shielding applications tends to be related to poor carbon-based nanoparticles dispersion during processing, considerably limiting EMI shielding performance enhancement by the combination of conductive nanoparticles addition and foaming [491]. That is why a lot of effort has be done in terms of improving dispersion of carbon-based nanoparticles, key in attaining the maximum effectiveness of the nanoparticles in terms of final material properties, but also important in critical foaming issues such as guaranteeing an efficient heterogeneous cell nucleation during foaming and hence proper control of the developed cellular structures [492].

In this sense, following some of the strategies previously presented in section "3.1.2. Effect of nanoparticle functionalization and/or surface modification", researchers have considered the functionalization of MWNTs prior to addition to epoxy in order to promote proper dispersion of CNTs during processing. Li et al. [492] have recently prepared epoxy-based microcellular foams containing functionalized MWNTs by means of sc-CO_2 foaming. As demonstrated by the authors, prior functionalization of the nanotubes improved their dispersion in epoxy, promoting an effective heterogeneous cell nucleation effect and leading to microcellular foams with comparatively smaller cell sizes and higher cell densities. As expected, microcellular foams displayed higher electrical conductivities and EMI SEs when compared to non-foamed nanocomposite counterparts (20.5 dB compared to 17.2 dB), which was once again related to the presence of the developed microcellular structure (enhanced absorbing capability), alongside an increase in the final thickness of the nanocomposite with foaming. As previously stated, besides enhanced EM absorption due to microcellular foaming, reorientation of the conductive nanoparticles around cell walls caused by foaming promoted a multiple wave reflection and scattering between the nanoparticles and cell-matrix interfaces, the combination of the two phenomena leading to an overall improvement of the EMI SE of the materials.

Pan et al. [493] used expandable microspheres to reduce the density of epoxy nanocomposites containing a combination of MWNTs and nickel-plated carbon fibres (NiCFs) and promote the formation of an effective conductive network, demonstrating the synergistic effect of the multiscale hybrid reinforcements (nanometric-sized MWNTs and micrometric-sized NiCFs – see Figure 43) in attaining specific EMI SE values as high as 72.6 dB·cm^3/g (compared to the 1.0-6.4 dB·cm^3/g of unfilled epoxy foam) at relatively low filler content (for further information about the use of multiscale hybrids consult section “2.4 Multiscale hybrids”).

Figure 43

5. Concluding remarks

This review summarizes the state-of-the-art and recent challenges in carbon-based polymer nanocomposites for EMI shielding applications, focusing on the theoretical models developed to predict the EMI shielding behaviour of these complex multiphase nanocomposites and mainly on the relation between the structure and processing of carbon-based polymer nanocomposites and respective cellular nanocomposites in terms of maximizing the EMI shielding efficiency. More specifically, the effects of the aspect ratio of the carbon-based nanoparticles (focusing on carbon nanotubes/nanofibres and graphene-based materials), their surface modification/functionalization, the effects of dispersion and possible preferential alignment throughout the polymer matrix during processing, the use of nanohybrids, multiscale hybrids and 3D carbon-based reinforcements, as well as the effects of polymer matrix morphology (phase(s) distribution, polymer microstructure, cellular structure) are considered and related to the dominant EMI shielding mechanisms (reflection, multiple reflection, absorption) and efficiency. All these aspects play a major role in the development of EMI shielding elements, increasingly required for avoiding problems of interference between electronic devices, with enhanced shielding characteristics when compared to common metals, besides obvious advantages of lower density, corrosion resistance and attained multifunctionalities.

From the viewpoint of the theoretical models developed to predict the EMI shielding behaviour of carbon-based polymer nanocomposites and avoid trial-and-error approaches, some have been developed based mainly on electrical conductivity, one of the main aspects of EMI shielding materials, others on the concept of EMI shielding efficiency, some others on modified parallel resistor-capacitor models, and some others on establishing multiscale hybrid systems.

Among models based on electrical conductivity the so-called electrical percolation model, which assumes an abrupt change in the behaviour of the material from insulating to (semi)-conductive at a critical conductive nanoparticle concentration (percolation threshold) has been the most commonly used, considering modifications based on the effects of possible nanoparticle’s orientation/alignment in the percolation threshold and electrical conductivity. Nonetheless, researchers have recently opted for mixed models that consider on the one hand possible conduction by percolation (physical contact between conductive nanoparticles, usually observed at moderate/high concentrations) and, under certain circumstances, tunnel-like conduction. Among these, tunnelling-percolation method (TPM) combined with the Two-Exponent Phenomenological Percolation Equation (TEPPE) has been proven fruitful to account for conductivity behaviours across the whole conductive nanoparticles concentration range. Only recently some researchers have extended the analysis considering the importance of conductor-insulator-conductor interface, with interesting results being observed by modelling possible interface effects by introducing in the model an interfacial conductivity assuming a "thinly-coated" nanoparticle, particularly to CNT [266] and graphene [272-273]. In this last case authors corrected the initial consideration of "graphene poor-graphene rich" domains by taking into account the presence of interfaces between the matrix and graphene using "coated-graphene" or "coated-graphene aggregates" instead of the original graphene layer or aggregate. Similar works have shown the importance of nanoparticle aggregate presence, one of the main causes of experimental electrical conductivities clearly below theoretical expected values, and even local nanoparticle deformation resulting from processing, in the electrical conductivity of the nanocomposite and hence EMI shielding. In this sense, as these novel models consider the presence of nanoparticle aggregate domains, they have also been proven useful to predict the electrical conduction performance of nanocomposites containing nanohybrids resulting from the combination of more than one type of nanoparticles, commonly CNT and graphene. Particularly, models have proven that the lowest possible percolation threshold is observed when combining a low amount of a high aspect ratio nanoparticle with a higher concentration of a lower aspect ratio one.

Additionally, authors have demonstrated that it is possible to predict in an easier way the EMI SE of nanocomposites using modified parallel resistor-capacitor models, directly relating a higher predicted electrical conductivity to a higher EMI SE (linear increase).

As carbon-based polymer nanocomposites are already materials with a multiscale morphology, this concept has been further extended to the modelling of nanocomposite systems containing multiscale hybrids, i.e., particles with different scale relations (nano and micro/macroparticles), researchers taking advantage of the most recent and previously mentioned models (tunnelling-percolation models that consider the importance of interface effects and particularly the presence of different conductive nanoparticle domains) to the tailor-made design of novel carbon-based nanocomposite elements with maximized EMI shielding properties.

In terms of the structure-processing relations of nanocomposites and respective cellular nanocomposites and how they can affect the EMI shielding properties and hence can be controlled to maximize them, a bigger importance has been given to the analysis of the effects of the morphology of the nanoparticles on the final nanocomposite, particularly the effects of nanoparticle dispersion and possible alignment during processing, the effects of nanoparticle aspect ratio and the possible use of nanohybrids, multiscale hybrids and 3D carbon-based reinforcements, without disregarding the importance of nanoparticle surface modification/functionalization (especially for improving dispersion and matrix interaction), with less focus on the influence of polymer matrix morphology.

Among the effects of nanoparticle dispersion, researchers have clearly shown that dispersion is crucial in attaining an effective conductive network at lower percolation thresholds, maximizing electrical conductivity and EMI SE. Different approaches have been considered to guarantee proper conductive nanoparticle dispersion in polymers: dispersion enhancement during processing, nanoparticle surface modification and functionalization prior to addition to avoid aggregation, and generation of polymer domains with controlled nanoparticle dispersion. From these, considerable research has been dedicated to the enhancement of nanoparticle dispersion during processing using melt-mixing methods, in-situ polymerization or solution-based methods, the last ones even considering the strategy of prior ultrasonication of the nanoparticles in solvents as a way to improve the dispersion. In terms of melt-mixing, a great deal of attention has been paid to the application of high local shear stresses, promoting the disentanglement of carbon nanotubes and partial exfoliation of graphene layers. Nevertheless, besides the possible partial rupture of the nanoparticles during processing and thus reduction of their aspect ratio, the re-aggregation of carbon-based nanoparticles is still a possibility, which has been limited by surface modifying and/or functionalizing the nanoparticles, additionally thought to enhance the interaction and compatibility with the matrix. The enhanced compatibility, while resulting in final nanocomposites with improved functionalities and enhanced electrical conductivities at lower percolation thresholds (optimization of the conductive network), has been shown by some authors to be counterproductive in some systems, as an excessive matrix-nanoparticle interaction has been proven counterproductive in maximizing the electrical conductivity and hence the EMI SE [346, 348]. Interestingly, researchers have recently contemplated a strategy to enhance the electrical conductivity of carbon-based nanocomposites based on the selective dispersion of the nanoparticles in a particular polymer phase, i.e., generating more complex polymer morphologies with polymer domains with controlled nanoparticle dispersion. With this thought in mind researchers were able to obtain nanocomposites with high electrical conductivities and high EMI SE at much lower nanoparticle concentrations by promoting a double percolation behaviour in which a lower amount of a nanoparticle-rich polymer phase (nanoparticles selectively localized in this phase by means of prior mixing or by promoting a higher affinity of this phase for the nanoparticles), acting as conductive domain, percolated the other polymer phase present in a higher amount [354-355], facilitating to a great extent the control of the dispersion of these conductive domains and as a result significantly reducing the percolation threshold and increasing the electrical conductivities, in some cases in more than 7 orders of magnitude.

Besides nanoparticle dispersion, crucial in defining the final morphology of the nanocomposite and electrical and EMI shielding properties, researchers have also shown the influence of the aspect ratio of the added nanoparticles as, assuming proper dispersion, nanoparticles having higher aspect ratios have been shown to lead to more effective conductive networks (lower percolation thresholds and higher electrical conductivities and EMI SE), as they increase the probability of formation of an effective conductive network at the same concentration of nanoparticles. Recent works have shown the viability of tuning the electrical percolation of nanocomposites by changing the relative concentrations of different carbon-based nanoparticles having different aspect ratios (two types of carbon nanotubes or graphene-based materials) or different morphologies (nanohybrids based on the combination of carbon nanotubes and graphene), enabling the development of high efficient pressure sensors.

Last but not least, further EMI shielding efficiency enhancements have been shown by some research groups when combining the strategy of adding conductive carbon-based nanoparticles with generating a cellular structure through foaming, as not only the significant density reduction would enable to extend the applicability of these materials to sectors where weight reduction is crucial such as aerospace, but also a controlled porosity would act as a strategy to selectively locate and disperse the conductive nanoparticles through the cell walls, reducing their average distance and hence optimizing the formation of an effective conductive network at lower nanoparticle concentrations. Also, the generation of a microcellular structure has been shown to promote multiple reflection as the main EMI shielding mechanism, as the larger cell-matrix interface areas, together with the layered structure of graphene and high aspect ratio of the carbon-based nanoparticles, promote the reflection and scattering of incident electromagnetic waves, trapping them until being dissipated as heat, hence significantly increasing EMI SE and extending their use to highly demanding electronics and aerospace applications.

As a final note, it has to be pointed out that the addition of different types of carbon-based nanoparticles to polymers and generation of a cellular structure through foaming enable to combine several multifunctional characteristics with the possibility of a tailor-made control of the EMI shielding properties, as the controlled assembly of the different phases and careful engineering of the interfaces in such multiphase materials would open new possibilities in a vast array of fields.

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Figure captions

Figure 1. Common EMI shielding materials and advantages of carbon-based polymer nanocomposites as alternative material.

Figure 2. North America nanocomposites market revenue according to type of nanoparticle. Adapted from [1].

Figure 3. CNT consumption in North America according to application. Adapted from [2].

Figure 4. Graphene market volume in the US according to type of graphene-based material. Adapted from [3].

Figure 5. Types of carbon-based nanoparticles: amorphous nanometric-sized carbon black (CB), single-wall carbon nanotubes (SWNT), multi-wall carbon nanotubes (MWNT) and graphene [5].

Figure 6. Schematic of filler dispersion using (a) latex technology and (b) dry-mixing method.

Figure 7. Morphology of (a) melt-extruded and (b) coagulated PC nanocomposites with 5 wt% SWNTs. Adapted from [202].

Figure 8. (a) Scheme of a cubic-like RVE for modelling the electrical conductivity of polymer-carbon nanotube nanocomposites (adapted from [248]) and (b) representation of conductive nodes between CNTs (adapted from [248]).

Figure 9. CNTs distributed in a rectangular parallelepiped (CNTs penetrating across the boundary surface appear in red). Adapted from [248].

Figure 10. Experimental results compared with the: (a) classical percolation model (Eq. 1), (b) TPM model, (c) TEPPE model and (d) combined TEPPE-TPM model. Adapted from [253].

Figure 11. Effect of nanofiller distribution and dispersion on the electrical conductivity of polymer nanocomposites. An effective electrical pathway is only guaranteed when the nanofiller is poorly distributed and properly dispersed (indicated in red).

Figure 12. Scheme of CNTs wall deformation in the radial direction as result of CNT separation below the van der Waals distance. Adapted from [282].

Figure 13. Scheme of multi-scale CNT percolation network model taking into account CNT aggregates. Adapted from [280].

Figure 14. Scheme of the cubic-like RVE used by Chen et al. [286] for polymer nanocomposites reinforced with CB-CNT hybrids and spherocylinder model used for CNT filler and sphere-like model used for CB aggregates.

Figure 15. Scheme of EM wave interaction (reflection, absorption and transmission) with a shielding material.

Figure 16. (a) Evolution of the ac conductivity of SWNT-reinforced polymer nanocomposites with SWNT concentration. The inset shows the parallel resistor-capacitor combination used to model σ_{ac}; (b) shielding efficiency evolution with σ_{ac} for different SWNT concentrations at 12.4 GHz. Adapted from [308].

Figure 17. Representation of various MWNT-polymer nanocomposites (MWNT: black, polymer: white) showing examples of conductive paths (dashed red line) and capacitance between the conductive path and adjacent MWNTs (grey): (a) high aspect ratio MWNT aggregates; (b) well-dispersed and aligned high aspect ratio MWNTs; (c)

well-dispersed and randomly-oriented high aspect ratio MWNTs; (d) lower aspect ratio MWNT aggregates; (e) well-dispersed and aligned lower aspect ratio MWNTs; and (f) well-dispersed and randomly-oriented lower aspect ratio MWNTs.

Figure 18. Multiscale hybrid for EMI shielding applications formed by a carbon nanotube-reinforced polymer foam inserted into an aluminium honeycomb. Adapted from [296].

Figure 19. Cross-section of a simplified rectangular cell of metallic honeycomb used in combination with a carbon nanotube-reinforced polymer foam (multiscale hybrid). For further information consult [316].

Figure 20. Scheme of MWNT modification from pristine MWNT to (a) lactic acid-grafted MWNT (LA-g-MWNT). Adapted from [341]; and to (b) oleic acid-modified MWNT. Adapted from [342].

Figure 21. Microstructural evolution of PEEK-PI-MWNT blends with increasing the proportion of PI (in all cases the concentration of MWNT was kept constant at 1 wt%). Adapted from [353].

Figure 22. Comparison between the (a) random distribution of CNTs in PA6-CNT nanocomposite and the (b) selective distribution of CNTs in PA6's phase in PA6-PP-CNT nanocomposite. Adapted from [355].

Figure 23. Schematic depicting the selective localization of CNTs in 90 PS/10 PA6/3.5 CNT nanocomposite (values in phr). Adapted from [357].

Figure 24. Micrographs of high aspect ratio graphene ((a) and (b)) and graphene nanoplatelets, xGnP ((c) and (d)) in PLA-based nanocomposites (graphene concentration: 0.56 vol%). Adapted from [366].

Figure 25. Comparison of simulated electrical conductivity and the experimental data of Wang and co-workers [372] measured parallel and perpendicular to the alignment of CNTs. Adapted from [371].

Figure 26. (a) Scheme of MWNTs alignment in epoxy nanocomposites and micrographs of MWNT networks in epoxy nanocomposites cured after (b) 5 min and (c) 15 min of electrical field application [374].

Figure 27. Alignment of 0.1 wt% CNFs in epoxy using an ac electrical field during (a) 0 min (randomly-oriented CNFs) and (b) 5 min (aligned CNFs). Adapted from [375].

Figure 28. Evolution of the electrical conductivity of CNF-reinforced epoxy nanocomposites as a function of CNF concentration considering randomly-oriented or aligned CNFs (in the case of aligned CNFs the electrical conductivity was measured parallel to CNF alignment) [375].

Figure 29. Evolution of the electrical conductivity of GnP-reinforced epoxy nanocomposites as a function of GnP concentration considering randomly-oriented or aligned GnPs (percolation threshold values are included for measurements done parallel to GnP alignment and assuming randomly-oriented GnPs) [370].

Figure 30. Evolution of SE with MWNT volume concentration for high aspect ratio MWNT-PDMS and lower aspect ratio SWNT-RET nanocomposites. Adapted from [301].

Figure 31. Scheme showing the three different MWNT-reinforced PE nanocomposite conductive networks prepared by Jia and co-workers [401]: (a) segregated MWNT structure (s-CNT/PE), (b) partially-segregated MWNT structure (p-CNT/PE) and (c) randomly-distributed MWNT structure (r-CNT/PE). SEM micrographs have been added on the right side (MWNT content: 0.8 wt%).

Figure 32. Variation of the shielding efficiencies with frequency due to (a) reflection (SE_R) and (b) absorption (SE_A), and (c) comparison between SE_R, SE_A and SE_{Total} at 10.3 GHz for the segregated MWNT structure (s-CNT/PE). Adapted from [401].

Figure 33. Scheme of PCL-MWNT nanocomposites preparation following the procedure of Bera et al. [351].

Figure 34. (a) Variation of SE with frequency for PCL-MWNT nanocomposites containing variable concentrations of MWNTs and (b) comparative SE values of PCL-MWNT nanocomposites containing 1.4 wt % and 1.8 wt % MWNT with PCL beads (70 wt %) and without PCL beads. Adapted from [351].

Figure 35. Representation of the different stages of nanohybrid preparation based on the combination of vertically-aligned MWNTs, Fe_3O_4 nanoparticles and rGO for EMI shielding enhancement of polymers proposed by Singh and co-workers [424].

Figure 36. (a) 3D printing of scaffolds by SC3DP method using a 200 μm inner diameter nozzle. (b) Three 4-layered printed scaffolds with different printed patterns and similar IFS, showing the transparency of the scaffolds. Adapted from [433].

Figure 37. (a) Schematic representation of nanofillers' alignment material deposition. (b) Optical image of a triangular honeycomb structure showing nanofiller orientation. Scale bar in (b): 500 μm. Adapted from [430].

Figure 38. Surface morphology of electrospun PVA-CNT composite nanofibres for different CNT concentrations: (a) 2.5 wt% CNT, (b) 5 wt% CNT, (c) 7.5 wt% CNT and (d) 10 wt% CNT. Adapted from [446].

Figure 39. TEM micrographs of (a) foamed PC-GnP nanocomposite and (b) unfoamed PC-GnP nanocomposite. Adapted from [456].

Figure 40. (a) Schematic description of electromagnetic wave transfer across PEI/graphene-Fe_3O_4 foams; (b) schematic diagram representing the multireflection route of electromagnetic wave between graphene-Fe_3O_4 sheets; (c) TEM image showing two parallel graphene-Fe_3O_4 sheets in the matrix as well as the possible reflection path of the electromagnetic wave. Adapted from [483].

Figure 41. Schematic for the fabrication procedure of porous PLA/MWNT with segregated MWNT networks and detail of the segregated MWNT conductive network formed at the boundaries of expanded PLA beads. Adapted from [474].

Figure 42. Representation of EM wave propagation across a PLA/MWNT nanocomposite foam. Adapted from [474].

Figure 43. Schematic of foaming and structural illustration of multiscale conductive network (reproduced with permission of Pan et al. [493]).

Table 1. EMI SE of MWNT-polymer nanocomposites in the X-band frequency range.

Polymer	Processing method	Sample thickness (mm)	MWNT (wt%)	EMI SE (dB)	Reference
PP	Melt-mixing	1	13.6	35.0	[396]
PS	Melt-mixing	2	10.0	50.0	[397]
ABS	Solution blending	1	10.0	40.7	[398]
PMMA	Solution blending	0.25-0.30	10.0	40.0	[399]
EMA	Solution blending – melt-mixing	2	10.0	20.0	[400]
UHMWPE	Wet mixing	1	10.0	50.0	[395]

Table 2. EMI SE of graphene-polymer nanocomposites in the X-band frequency range.

Polymer	Graphene (wt%)	Sample thickness (mm)	EMI SE (dB)	Reference
PMMA	5.0	3.4	25.0	[406]
PU	7.7	2.0	35.0	[407]
PS	10.0	2.8	18.0	[408]
PS	7.0	2.5	45.1	[409]
PEDOT-PSS	10.0	0.8	46.0	[410]

Table 3. Comparison of EMI and electrical conductivity measurements of different polymer foams reinforced with carbon-based nanofillers.

Matrix	Nanofiller	Foaming process	σ_{max} (S/m)	EMI SE (dB)	Specific EMI SE ($dB \cdot cm^3 \cdot g^{-1}$)	Main EMI shielding mechanism	Ref.
PU	CNT	In situ	2.03×10^{-6} @ 1.2 wt%	-		-	[467]
PU	TRGO [a]	CO_2	-	-	15.15 @ 0.3 wt%	Absorption	[468]
PMMA	Graphene	sc-CO_2	3.11 @ 5 wt%	13.0-19.0 @ 5 wt%	17.0-25.0 @ 5 wt%	Absorption	[459]
PVDF	TRGO [a]	Chemical	10^{-4} @ 0.5 wt%	20 in X-band / 18 in broadband @ 5 wt%	-	Reflection	[462]
PS	Graphene	sc-CO_2	1.8×10^{-2} @ 20 wt%	18 @ 10 wt%	-	Absorption	[469]
PS	Graphene	Compression moulding and salt-leaching method	1.25 @ 30 wt%	29.3 @ 30 wt%	64.0 @ 30 wt%	Absorption	[454]
PP	CNT	sc-CO_2	3.93 @ 5.47 vol%	45-50 @ 0.184 vol%	-	Absorption	[470]
PEI	TRGO [a]	Phase separation	1.08×10^{-8} @ 0.39 vol%	20 @ 10 wt%	44 @ 10 wt%	Absorption	[453]
PI	rGO/CNT	Solvent evaporation	1.87 @ 8 wt%	18.2 @ 8 wt%	41.4 @ 8 wt%	Absorption	[471]

		induced phase separation					
PI	rGO	Non-solvent induced phase separation	1.0 @ 16 wt%	21.0 @ 16 wt%	75.0 @ 16 wt%	Absorption	[472]
PCL	CNT	sc-CO_2	4.0 @ 0.25 vol%	80.0 @ 0.25 vol%	258.0 @ 0.25 vol%	Absorption	[320]
PLLA	CNT	sc-CO2	3.4 @ 10 wt%	23.0 @ 10 wt%	77.0 @ 10 wt%	Absorption	[473]
PLA	CNT	Expandable bead foaming	10.0 @ 0.0054 vol%	50.0 @ 0.0054 vol%	1010.0 @ 0.0054 vol%	Absorption	[474]

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[a] Thermally reduced graphene oxide