A review concerning the main factors that interfere in the electrical percolation threshold content of polymeric antistatic packaging with carbon fillers as antistatic agent

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Abstract
The use of high contents of carbon fillers in polymeric composites may decrease the mechanical properties of the polymeric matrices, as well as reduce their processability and increase the production costs of antistatic packaging used in the electronic industry. Therefore, it is of great technological interest the research on alternative approaches to produce polymer composites with low electrical percolation threshold. In this way, this review article focuses on the discussion of the main factors that interfere in the electrical percolation threshold of electrically conductive polymer composites, such as the aspect ratio of the carbon fillers and its particle size, the compatibility between the composite phases, the crystallinity degree of the polymeric matrix, the processing route and the location of fillers in multi-phase polymer blends. Additionally, the review article reports the latest studies related to the obtainment of polymer composites with low percolation threshold contents and produced with different types of carbon fillers.

KEYWORDS
carbon-based antistatic agents, electrical percolation threshold, polymer antistatic packaging

1  |  INTRODUCTION

Electronic devices are generally sensitive to electrostatic discharge (ESD) generated by friction (triboelectricity) during handling, packaging, and transportation processes in the electronic industry, being possibly totally damaged.[1,2] The protection of electronic devices against ESD is of great importance in the electronic industry, preventing a decrease in the production yields, avoiding an increased warranty rework, and guaranteeing plain customer satisfaction by offering durable and high-quality products.[3]

In this way, the ESD protection of electronic devices requires the use of a special package called antistatic packaging, which must present low electrical resistivity to avoid electron accumulation and facilitate the flow of electric charges through its structure.[4] Electrically insulating materials present a relatively high surface resistivity (>\(10^{11}\) \(\Omega\) \(\cdot\) \(\text{s}\)), indicating that the electron flow is hampered through its surface.[5] This problem does not
occur in materials with antistatic and dissipative properties, since their electrical resistivity \((10^4 - 10^{11} \, \Omega \, \text{sq}^{-1})\) is low enough to permit electronic conduction. In turn, materials with electrical resistivity smaller than \(10^4 \, \Omega \, \text{sq}^{-1}\) (such as many carbon materials and metallic particles) are classified as conductive materials and are intensively utilized in the production of polymer composites for antistatic applications.\(^5\)

Polymeric matrices are the best alternatives for the production of antistatic packaging considering their inherent lightness and good processability.\(^6\) Nonetheless, most polymers are insulator materials, so it is necessary to modify their formulation to impart dissipative properties to their structures. Usually, this modification is performed by the addition of organic compounds like ionic and non-ionic surfactants or by the addition of electrically conductive particulate fillers.\(^7\) These polymer modifiers are generally called antistatic agents. The migration of surfactant molecules to the surface layer of the polymer generates a hydrophilic coating on the material due to the exposure of their oxygen functional groups, absorbing water from the atmosphere and imparting antistatic properties to the polymer.\(^8\) In this way, a negative issue related to this approach is the dependence of the antistatic packaging effectiveness on the relative humidity of the air.\(^9\) Besides, over time the surfactant molecules deteriorate on the surface, which may negatively interfere with the dissipative properties of the packaging.\(^8\)

On the other hand, the addition of electrically conductive particulate fillers (such as metal or carbon nanoparticles) on electrically insulating polymeric matrices constitutes an interesting alternative way to impart permanently good electrical properties to the material.\(^10,11\) When a critical amount of antistatic agent particulate (called electrical percolation threshold content) is added to polymeric matrices, the electrically conductive particles physically get in touch with each other forming electron-conductive paths inside the polymer composites, permitting electronic flow and the consequent increase of many decades of magnitude in the polymer electrical conductivity (Figure 1).\(^12-14\) The charge flow inside polymer composites may also occur by tunneling between sufficiently close conductive particles (<10 nm). The tunneling effect may be considered as a predominant electron-conduction mechanism when it is observed a power law current-voltage (I-V) relationship for the material. On the other hand, when it is verified a linear I-V relationship, probably the direct contact between the filler particles plays a major role in the electronic conductivity.\(^15\)

Particulate carbon materials are intensively used as antistatic agents for the production of antistatic packaging since they possess high electrical conductivity, mechanical resistance, low thermal expansion, and good corrosion resistance.\(^16\) Besides, the addition of such materials may diminish the water vapor permeability of the polymer by increasing the tortuosity path for the diffusion of water molecules, conferring better protection for electronic components sensitive to moisture.\(^17\) Among the carbon materials used as antistatic agents, it is possible to mention CNTs,\(^18\) carbon black (CB),\(^19\) glassy carbon (GC),\(^20\) graphene,\(^21\) and graphite/graphene nanoplatelets (GNP).\(^22\)

The particles of antistatic agents have different shapes. The graphene consists exactly of an individual sheet of graphite, being, therefore, a two-dimensional material.\(^23,24\) The structure of CNTs can be described as a rolled graphene sheet, forming tubes of nanometric diameters with properties depending on both the diameter and how these tubes wind up.\(^25\) Also, different sheets can be rolled up concentrically, separated by distances similar to the separation of graphene sheets in graphite, giving rise to multi-walled carbon nanotubes (MWCNT).\(^26,27\) The CB is characterized by spherical graphitic particles, that normally aggregate to form larger ellipsoid structures.\(^28\) The GC is very brittle and presents a surface fracture similar to that presented by the glass, which explains the “glassy” denomination.\(^29,30\) Due to its brittleness, GC particles present smooth surfaces and straight edges and furthermore can be almost isometrically shaped.\(^31\)

The use of high contents of carbon fillers (especially in the non-functionalized form) in polymer composites may decrease the mechanical properties of the polymeric matrix, as well as reduce its processability and increase the production costs of antistatic packaging due to the

![Figure 1](image-url)
relatively elevated price of some carbon materials, such as CNT and graphene.\cite{12,32–34}

Therefore, it is of great technological interest the research on alternative approaches for the production of polymer composites with low electrical percolation threshold, permitting the obtainment of antistatic packaging with attractive overall properties at low cost.

In this way, this review article focuses on the discussion of the main factors that interfere in the electrical percolation threshold of electrically conductive polymer composites, such as the aspect ratio (AR) of the carbon fillers, the particle size, the compatibility between the composite phases, the crystallinity degree of the polymeric matrix, the processing route and the localization of fillers in multiphase polymeric blends. Additionally, the review article reports the latest studies (2017–2020) related to the obtainment of antistatic packaging with low electrical percolation threshold contents.

2 FACTORS THAT INTERFERE IN THE ELECTRICAL PERCOLATION THRESHOLD CONTENT OF ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES

Different factors may influence the electrical percolation threshold of electrically conductive polymer composites used for antistatic packaging and are systematically discussed in the next subsections.

2.1 Compatibility between the phases of polymer composites

The chemical compatibility between the polymeric matrix and the antistatic agent in polymer composites has a strong influence on the electrical percolation threshold of the antistatic packaging, since a good interaction between the composite phases facilitates the dispersion of the conductive fillers in the material, favoring the formation of electron-conductive paths (Figure 2).

The improvement in the compatibility between the matrix and the antistatic agent in polymer composites may be achieved by performing chemical and/or physical modifications in the surface properties of carbon fillers, especially for CNTs and graphene.\cite{35} In the covalent functionalization, different polar functional groups (such as carboxylic acid, ketone, alcohol, and ester groups) are attached by covalent bonds to CNTs caps and their sidewalls, improving the interaction between the carbon particles and the polymeric matrix inside the composite. The chemical functionalization may be performed by using oxidative treatments with strong acids (e.g., HNO\(_3\) and H\(_2\)SO\(_4\))\cite{36} and bases (NaOH)\cite{37} or with strong oxidants like ozone and ultraviolet radiation.\cite{38}

The non-covalent functionalization of CNTs, in turn, involves the obtainment of non-covalent modifications on the surface of the nanofiller. For this process, it is commonly used surfactant molecules,\cite{39,40} and conjugated polymers capable of establishing \(\pi-\pi\) stacking or hydrophobic interactions with CNTs sidewalls.\cite{41}
factants molecules, for example, may reduce the surface tension of CNTs and generate electrostatic/steric repulsive forces between nanofiller particles, reducing the effect of van der Waals forces and preventing CNT bundling. [35]

Soares et al. [42] produced polypropylene (PP)/poly(lactic acid) (PLA) (70/30) blends reinforced with pristine CNT or non-covalently functionalized CNT (CNTf) with alkyl phosphonium-based ionic liquid by melt processing. It was verified by transmission electron microscopy (TEM) that CNTf were better dispersed in the PP/PLA matrix when compared with pristine CNT, which was attributed to the physical interaction between the ionic liquid molecules bound in the CNT surface and the PP polymer chains, promoting the debonding of the nanofiller aggregates and the good CNT dispersion in the composite. Electrical measurements indicated that the percolation threshold in PP/PLA blend was obtained with 0.003 volume fraction of pristine CNT, while in the nanocomposites reinforced with CNTf the insulating-conducting transition occurred in the $6 \times 10^{-4}$ and $2 \times 10^{-3}$ volume fraction range, evidencing the better dispersion of CNTf in the dissipative material.

Aranburu et al. [21] verified the influence of the addition of graphene functionalized with ionic liquid (graphene-IL) on biobased thermoplastic polyurethane (bTPU). The main goal of using IL in graphene was to reduce the agglomeration of graphene sheets in the polymeric matrix, to improve the electrical properties. The IL used was the 1-butyl-3-methylimidazolium tetrafluoroborate. In order to verify the effect of modification in graphene, composites of bTPU/graphene (0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 wt% of graphene) and bTPU/graphene-IL (1.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, and 7.0 wt% of graphene-IL) were produced by melting processing in a twin-screw extruder. Despite incomplete exfoliation of graphene, it was verified an increase in the electrical properties, which may be attributed to an adequate dispersion of the graphene and graphene-IL in bTPU. The electrical percolation threshold ($10^{-7}$ S cm$^{-1}$) was calculated using a Power Law function and was achieved with 1.99 wt% graphene-IL and 3.21 wt% graphene. In this way, the functionalization of graphene contributed to the decrease in the electrical percolation threshold of the composites.

The dispersion of functionalized carbon nanofillers in a certain polymeric matrix may be notably improved by using chemically modified macromolecular chains of the same polymer in the composite, designated as a compatibilizer agent. The modification of the polymeric matrix may be performed by grafting different molecules to the macromolecular chains, such as acrylic acid (AA) and maleic anhydride (MAH), [18] which increases the polarity of the polymer and facilitates its interaction with different fillers.

According to Braga et al. [16] the reactive extrusion processing constitutes an effective way to prepare MAH grafted poly(trimethylene terephthalate) (PTT) (PTT-g-MAH). The compatibilizer agent was used in PTT/acrylonitrile butadiene styrene (ABS) (PTT/ABS) blends and PTT/CNT nanocomposites, improving the thermal and mechanical properties of these materials that can be used as antistatic packages.

### 2.2 Electrical conductivity of the antistatic agent particles

As expected, the electrical conductivity of carbon filler particles plays an important role in determining the electrical percolation threshold of electrically conductive polymer composites. The electrical conductivity of the carbon-based nanocomposites depends on the intrinsic characteristic of the carbon filler. The inherent electrical conductivity of carbon fillers is being already studied, despite its interpretation is still a challenging task. [23,43–45] Generally, the electrical conductivity of the bulk powder is lower than the single-particle, because the interface between the particles offers extra resistance for electric charge transport, moreover, the bulk conductivity is affected by the number of particles contact and the packing density. [46] In an interesting study made by Marinho et al. [46] the authors reported the difference in the electrical behavior of four different carbon particles: MWCNT, graphene, graphite, and CB. For anisometric materials (MWCNT, graphene, and graphite), the conductivity behavior, considering filler power compaction (which depends on the packing density), is governed by the mechanisms of rearrangement and fragmentation of agglomerates particles; and for CB, it is governed by increasing the particle contact area.

The electrical conductivity of carbon fillers, in turn, may also be related to the perfection degree in the arrangement of conjugated chemical bonds established by their carbon atoms. For example, graphene oxide (GO) is a graphitic carbon material commonly obtained by the oxidation of pristine bulk graphite and may be easily exfoliated in hydrophilic solvents (e.g., water) due to its polar surface functional groups like carboxyl, hydroxyl, and carbonyl groups. [47] Nevertheless, the formation of these functional groups after oxidation processes and the partial destruction of the conjugated structure increases the electrical resistivity of graphite sheets (Figure 3), which may be reversed by submitting the material to reduction processes producing the so-called reduced graphite/graphene oxide (rGO). [48] This carbon filler presents good electrical conductivity ($1.2 \times 10^2$ S m$^{-1}$) and therefore constitutes a good alternative of antistatic agent for polymer composites.

For example, Xue et al. [49] produced poly (L-lactic acid) (PLLA)/expanded graphite (EG) composites by melting
processing using an internal mixer. It was verified in the PLLA/EG samples previously submitted to in situ reduction of EG a lower electrical percolation threshold (7.1 wt%) than that observed for the PLLA/EG composites not submitted to the reduction treatment (11.2 wt%). These results were attributed to the reduction of the oxidizing ion groups present in EG and the recovery of its full conjugated structure.

As mentioned previously, the covalent functionalization of CNT constitutes an excellent strategy to improve interfacial bonding of the filler with polymeric matrices, involving the formation of a high density of oxygen functional groups that are capable to interact with polymeric chains and thus increasing the carbon filler dispersion in the polymer composite. Nevertheless, chemical functionalization may lead to the opening of the tube caps on CNT, to the formation of holes in the sidewalls, and to the shortening of the nanotubes (especially when accompanied by ultrasonication treatment), decreasing their AR.\(^{[35,37]}\) Besides, covalent functionalization leads to a localized change of carbon hybridization, from \(sp^2\) to \(sp^3\), forming structural defects that decrease the mechanical properties of CNTs. The resultant partial destruction of the conjugated chemical structure of graphitic structures may also impair the mechanism of electron transport, decreasing the electrical conductivity and disturbing the formation of a continuous conductive-electron network inside the nanocomposite, which may increase the electrical percolation threshold.\(^{[50,51]}\)

Braga et al.\(^{[52]}\) developed PTT/CNT nanocomposites for antistatic packaging and evaluated the influence of the CNT functionalization (with nitric acid) on the electrical properties of the materials. The authors verified that the nanocomposites with 0.5 or 1 wt% of functionalized-CNT presented higher values of electrical resistivity when compared with the values presented by the nanocomposites with the same content of pristine CNT. This result may be attributed to the partial destruction of the conductive graphitic structure of CNT caused by the utilization of strong acid in the functionalization. In another work, Braga et al.\(^{[53]}\) studied the influence of functionalized-CNT on the properties of the PTT/ABS blend. The addition of 0.5 wt% of functionalized-CNT in the polymeric blend decreased the electrical resistivity only by one decade of magnitude when compared with the PTT/ABS blend. As the functionalized-CNT content increased to 1 wt%, the electrical resistivity decreased by five decades of magnitude, reaching \(10^5 \Omega \cdot \text{cm}\). The reduction in the electrical resistivity was not as steep as that observed with the use of pristine CNT because the chemical oxidation process produced structural defects in CNT, impairing the mechanism of electron transport.

The non-covalent functionalization of carbon fillers, in turn, does not lead to the destruction of the conjugated chemical structure, preserving the overall properties of the material.\(^{[35]}\) According to Guadagno et al.,\(^{[54]}\) the non-covalent functionalization of MWCNTs may represent an interesting strategy to conserve its graphitic structure, preserving the electrical properties and making possible the obtainment of low electrical percolation thresholds. The authors suggested the use of 1-pyrenebutyric acid for MWCNT functionalization and did not verify any decrease in the performance of the nanocomposites produced with functionalized-MWCNT, regarding their electrical properties. Moreover, no increase in the electrical percolation threshold nor decrease in the electrical conductivity were observed when considering the nanocomposites containing pristine MWCNT.

### 2.3 AR of the antistatic agent particles

AR may be defined as the ratio between the longest dimension of a filler particle and its smallest dimension.\(^{[55]}\) The
AR value may be used to quantitatively describe the shape of a filler particle. The more spherical is the particle shape, the more the AR value approximates to zero. On the other hand, filler particles with platy (such as GNPs) or fibrous shape (e.g., CNT) present high AR values (as high as 3700). Many researchers have correlated the obtainment of low values of electrical percolation threshold in polymer composites with the use of fillers presenting high AR. Elongated cylindrical particles may form an interconnected network of electron-conductive fillers inside polymer composites more easily than spherical ones, favoring the obtainment of dissipative properties, as observed in Figure 4. Furthermore, fillers with higher AR values present higher surface area (when comparing particles with the same volume), making possible a greater stress transfer from the polymeric matrix to the reinforcing phase and imparting good mechanical properties to the antistatic packaging.

Xiang et al. prepared by melting processing nanocomposites of high-density polyethylene (HDPE) filled with different carbon-based fillers (GNPs, CB and MWCNT), using single or binary combinations of fillers at the total content of 4 wt%. The rheology and electrical resistivity tests indicated that the relative efficiency in the generation of rheological and electrical conductive networks occurred in the MWCNTs > CB > GNPs order, while the increase in the elastic modulus was achieved in the GNPs > MWCNTs > CB order, considering equal filler contents.

Kunz et al. evaluated composites of different polymeric matrices (poly (vinylidene fluoride) (PVDF), polyamide 6 (PA6), and ABS) reinforced with different carbon fillers such as CB, graphite, EG, branched MWCNT (b-MWCNT), non-branched MWCNT (MWCNT), and single-walled carbon nanotubes (SWCNTs). The composites were produced by melting processing followed by film extrusion or compression molding. To study the influence of this different processing, the authors focused on the study of the PVDF composite with MWCNT (2 wt%), b-MWCNT (1 and 2 wt%), and CB (4 wt%), since they presented different electrical conductivity in both processing. A strong alignment of all the fillers was observed in compression molding composites. Additionally, the use of b-MWCNT promoted the obtainment of higher electrical conductivity values than MWCNT and CB due to its branches, which contributed to the formation of an electron-conducting network. A higher electrical percolation threshold of composites with CB was observed. The film extrusion induced an even stronger orientation of b-MWCNT in the composites promoted by the melt flow and the take-off forces during the process.

The use of particulate material with distinct AR values usually makes possible the obtainment of lower percolation thresholds in polymer composites than the use of antistatic agent particles with similar AR values. This synergistic effect may be explained by the complementary effect established between more elongated particles, which act as electron carriers, and particles with lower AR, which fill the spaces between more elongated particles facilitating the formation of electrical conduction.

Ge and Deva developed polyvinyl alcohol (PVOH) nanocomposites reinforced with a hybrid filler system (CB and GNP) for ESD application, varying the GNP/CB content (2, 4, 6, 10, 12, and 14 wt%) and the GNP/CB ratios (10:90, 30:70, 50:50, 70:30, 90:10). These nanocomposites were prepared by solution processing being posteriorly conformed into films by the compression molding process. These films were analyzed by evaluating the surface and volumetric resistivity. It was verified that neither polymeric compositions reinforced with one single filler (GNP/CB ratios of 100:0 and 0:100) presented a reduction in the electrical resistivity, even at high GNP/CB contents (up to 14 wt%), which may be attributed to insufficient dis-
persion of the filler particles inside the polymeric composites due to van der Waals forces. On the other hand, polymeric compositions with GNP/CB ratios of 10:90 and 30:70 presented a decrease of seven decades of magnitude in the electrical resistivity, with percolation thresholds of 8–10 wt% GNP/CB. Probably, CB particles filled the space between GNPs, avoiding GNP entanglement, and facilitating the attainment of electrical conduction.

2.4 Particle size of the antistatic agent

The particle size of the antistatic agent particles has a strong influence on their distribution in the polymeric matrix of polymer composites. The same weight content of a certain nanoscale material presents many more particles than the same weight content of the same material with macroscale particles, which may facilitate the distribution of the carbon filler in polymeric composites. In this way, the use of nanofillers makes possible the attainment of polymer composites with remarkably low electrical percolation threshold and high electrical conductivity values, which is not usually achieved by using micro-sized antistatic agents. By way of example, the use of graphite microparticles in conductive composites may be interestingly replaced by the use of other similar carbon materials that present nanoscale particles, such as graphene, rGO, and GNP.

Besides, nanoparticles possess a much higher surface area than microparticles, implying greater interaction with polymeric chains, better stress transfer from the polymeric matrix to the reinforcement phase, and increased mechanical properties in polymer composites. The use of nanoparticles may also be efficient in the attainment of antistatic materials with reduced water vapor permeability, conferring good protection to electronic components that are sensitive to humidity.

Figure 5 shows the effect of the filler particle size on its distribution on the polymeric matrix in polymer composites.

2.5 Crystallinity degree of the polymeric matrix

The crystallinity degree ($X_c$) of the polymeric matrix used in the production of the antistatic packaging also interferes with the electrical percolation threshold of the polymeric composites. It has been verified that many antistatic agents (such as CB) tend to be located in the amorphous region of the polymeric matrix in composites. In this way, the increase in the $X_c$ value decreases the proportion of the amorphous phase in the polymer and favors physical contact between the carbon particles, forming an electrical percolation path with lower contents of the antistatic agent (Figure 6). Differently from CB, other antistatic carbon fillers like MWCNT and graphene may present crystallite nucleation effect on different polymeric matrices, increasing the $X_c$ value and influencing the electrical conductivity.

Weidenfeller et al. prepared polyamide 46 (PA 46)/CB composites with 10 v%, 20 v%, and 30 v% CB by melt processing, and posteriorly performed thermal treatment in the materials at 126°C for different periods. The authors verified that the compositions with the addition of 10 v% CB presented a decrease of 9 decades of magnitude in volume resistivity after 128 hours of annealing, ranging from $1 \times 10^{13} \Omega \text{mm}$ to $5 \times 10^{14} \Omega \text{m}$, which was attributed to the decrease in the polymeric crystallite size, to the improvement in the level of crystallite perfectness, and the increase
The higher crystallinity degree led to a decrease in the space for CB in the amorphous region, facilitating physical contact between the particles and the formation of electron-conductive paths. Besides, with annealing for 64 hours, the electrical percolation threshold of PA 46/CB composites decreased from \( \sim 20 \) wt\% to \( \sim 10 \) wt\%, confirming the effectiveness of thermal treatment in the electrical properties of the material.

Wang et al.\cite{72} prepared PP/CNT nanocomposites by melting processing followed by compression molding and verified a decrease in the electrical percolation threshold contents of the materials with the increase in the degree of crystallinity on the polymeric matrix. The authors attributed this result to the use of a slow cooling rate during the compression molding, which favored the formation of large polymeric crystallites and the obtainment of a volume exclusion effect on the CNT, forming a selectively distributed structure of antistatic agent particles on the PP amorphous phase.

### 2.6 Processing route

Another relevant factor that determines the electrical percolation threshold is the processing route used for the dispersion of the antistatic agent in the polymeric matrix, especially when the particles are in the nanoscale.\cite{78} The melting processing, represented by conventional methods such as injection and extrusion processing, make possible the industrial-scale processing of polymeric composites at a competitive cost by controlling the temperature, pressure, and shear stress on the polymer, resulting in the melting/softening of the material and the dispersion of the carbon filler in the polymeric matrix.\cite{79} Nevertheless, the viscosity of the polymer/filler system increases markedly with the increase in the antistatic agent content, making difficult its dispersion.

The solution processing (also designated as solution-casting or solution blending), constitutes an interesting alternative to the melting processing method, in which the antistatic agent particles may be stirred (generally by sonication) and mixed in the polymeric matrix previously dissolved in a chemically compatible solvent.\cite{80} This method allows the obtainment of a low viscosity medium, facilitating the filler dispersion in the composite resulted after the evaporation of the solvent.\cite{81} Nevertheless, the sonication of carbon antistatic agents may lead to the breakage of elongated nanofillers and the decrease in their AR when performed in severe conditions (for a long time and great power), which may increase the percolation threshold in the polymer/nanofiller system.\cite{82}

Luo and Schubert\cite{78} obtained poly(methyl methacrylate) (PMMA)/graphene nanoplatelet composites by using melting and solution processing, prepared the samples by compression molding, and evaluated the effect of the different processing routes on the electrical properties of the materials. The authors verified that the composites obtained by solution processing presented lower electrical percolation threshold values (0.89 vol\%) when compared with the composites obtained by melting processing (2.32 vol\%). Probably, the low viscosity medium obtained by solution processing facilitated the exfoliation of graphene sheets, permitting better dispersion of the carbon-based nanoparticles on the polymeric matrix, as shown by morphological analysis.
Another processing technique used to obtain polymer composites is in situ polymerization, which consists of the polymerization of monomer molecules in the presence of filler particles.\cite{83,84} This method constitutes an interesting alternative to solution and melting processing methods, especially when thermally unstable or insoluble polymeric matrices are used.\cite{85–87} The schematic diagram of Figure 7 shows the possible processing routes for the production of polymeric composites for antistatic applications.

Since melting processing makes possible the industrial-scale production of polymer composites at a competitive cost, many studies have been conducted on the use of this technique for the production of polymer composites with carbon-based fillers.\cite{88} For example, Ezat et al.\cite{89} verified that the screw configuration of the extrusion process also has an important effect on the dispersion of nanofillers in polymer nanocomposites. The authors prepared PP/MWCNT samples with different MWCNT contents (0, 2, 4, 6, 8, 10, and 12 wt% MWCNT) by extrusion processing, and varied the screw configuration by changing the type and position of screw elements in the mixing and melting zones. It was verified that the use of a screw configuration containing kneading and reverse-conveying elements made possible the obtainment of PP/MWCNT nanocomposites with the higher degree of MWCNT dispersion in the polymeric matrix and with the lowest electrical percolation threshold (2 wt%) when compared with the PP/MWCNT nanocomposites produced by using folding elements or without using reverse-conveying elements (6 wt%). The authors indicated that the use of reverse-conveying elements makes possible the increase in the residence time and the obtainment of a high intensity mixing with the generation of high stress during melt processing, diminishing MWCNT agglomeration by van der Waals interaction.

Sui et al.\cite{90} evaluated the influence of the screw rotation speed in a twin-screw extruder on the dispersion of MWCNT in an olefin block copolymer (OBC) matrix. It was verified that the entangled agglomerates of MWCNT could be easily destroyed by using high rotation speed and improved dispersion of MWCNT was observed by increasing the screw rotation speed from 50 to 500 rpm. However, a further increase in the screw rotation speed from 500 to 1000 rpm led to the reduction of the MWCNT length; besides, it was not obtained a better dispersion of the nanofiller in the polymeric matrix. As a result, the best electrical conductivity and mechanical properties of OBC/MWCNT composites were achieved by using the screw rotation speed of 500 rpm, obtaining an electrical percolation threshold of about 1.5 wt%.

Reactive extrusion is another way to achieve a low electrical percolation threshold in polymer composites due to its high capacity of molecular mixing. Ozdemir et al.\cite{22} studied the effects of the use of reactive extrusion in polyethylene terephthalate (PET)/GNP composites (0.25, 1, 3, 5, and 10 wt% GNP) and PET/copolymer of ethylene methyl acrylate (EMA) (2 wt %) blend–based GNP nanocomposites (0.25, 1, 3, 5, and 10 wt% GNP). Fourier-transform infrared spectroscopy (FTIR) and dynamic oscillatory rheology analysis showed the trans-esterification reaction between PET and EMA occurred during the reactive extrusion forming a crosslinked structure that formed a three-dimensional network between GNP particles, which lowered the electrical percolation threshold content of the composite when compared with the materials without EMA. The presence of the crosslinked structures

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**Figure 7** Schematic diagram indicating the possible processing routes for the production of polymer composites for antistatic applications.
increased the melt strength and the shear forces of processing, leading to a higher GNP dispersion in the polymeric matrix. It was verified that, the higher shear force, the higher the GNP dispersion and the lower the electrical percolation threshold of the composites, which was achieved with 3 wt% GNP for PET/GNP (σ = 6.07 × 10⁻⁷ S cm⁻¹) and 1 wt % GNP for PET/EMA/GNP (σ = 9.7 × 10⁻⁷ S cm⁻¹) blend-based composites.

In the study of Thi et al. [91] it is possible to verify that the orientation distributions of the nanofillers (CNT, CB, and carbon fibers) after the injection molding process reduce the interparticle contacts between particles and thus decrease the electrical conductivity. Thus, the authors suggest a new methodology using post-processing annealing to obtain better values of electrical conductivity.

Yazdani et al. [92] verified the influence of the processing method on dispersion quality, electrical conductivity, and mechanical properties. The authors observed that the composite samples using an optimum combination of power and duration in the probe sonication method yielded the lowest percolation threshold with the highest overall electrical conductivity and statistical consistency among all of the methods examined.

Yuan et al. [93] prepared CNT composite powders and utilizes them for the selective laser sintering (SLS) process. Because through this process it is possible to obtain composite with electrically conductive segregated structures when comparing with the hot-compression process, the SLS process could offer an effective method to fabricate the CNT/polymer composite with good electrical properties.

2.7 Morphology of the polymeric matrix on blends

The last consideration to be made about the factors that affect the electrical percolation threshold is related to the amount and the morphology of the phases present in the material, especially when it comes to composites of polymer blends [94]. The production of polymer blends constitutes a suitable and economic strategy to modify polymeric matrices by balancing their mechanical properties (like impact strength), reducing costs, and improving processability [95]. Different factors may influence the electrical percolation threshold of polymer blends, such as the blend ratio, the phase morphology, and the location of the carbon filler inside the material.

The physical mixing of two immiscible polymers in the production of polymer blends may lead to the formation of a material with a continuous and dispersed phase or to the formation of a material with two co-continuous phases. The addition of antistatic agent particles that preferentially are located in a continuous phase or at the interface between two co-continuous phases in immiscible polymer blends may favor the establishment of physical contact between the particles and facilitate the formation of an electron-conducting path in the composite, thus lowering its electrical percolation threshold [96–98]. The selective distribution of the filler particles in the interfacial region or in a single phase of co-continuous polymeric blends (generating a network of conductive particles) and the formation of a conductive network of filler-rich polymeric phase inside the composite is designated as double percolation [99]. This phenomenon was firstly described by Sumita et al. [100] for HDPE/PP and PMMA/PP blend-based CB composites. Figure 8 shows the effect of the selective localization of carbon filler particles on the electrical percolation threshold of blend-based polymer composites.

The filler selective location phenomenon and the double percolation threshold in polymer blends were studied by Lu et al. [88]. The authors focused on the obtainment of PLA/recycled HDPE (70/30) blend-based CB composites with a co-continuous morphology and selective location of CB on the HDPE phase, employing the melting processing method. The use of this strategy made possible the reduction of the electrical percolation threshold from 15 wt% CB in neat HDPE to 5 wt% CB in PLA/HDPE blends.

The electrical percolation threshold of polymer composites may also be reduced by stereocomplex crystallization on miscible polymer blends. The stereocomplex crystallization phenomena occur, for instance, in both PLA enantiomers (PLLA and PDLA), which crystallize side by side forming a racemic crystallite also called stereocomplex (SC). The SC presents higher mechanical properties and melting temperature than the holocrystalline PLLA or PLDA [102]. Liu et al. [103] prepared PLLA/PLDA blend-based CB composites by melting processing, with different PLLA/PLDA blend ratios (99/1, 98/2, and 90/10). As a result, for the PLLA/PLDA (99/1) blends the formation of SC increased the melt viscosity of the matrix facilitating the CB agglomerates dispersion and reducing the electrical percolation threshold when compared with the PLLA/CB composites. However, for higher PLDA contents the SC formation acted as a physical barrier.

Yang et al. [99] produced PVDF/ polystyrene (PS) (45/55) blends with different volume content (0.05, 0.09, 0.18, and 0.36 vol%) of pristine CNT or CNT grafted with PMMA chains (CNTs-PMMA). The authors verified that non-modified CNT was selectively distributed on the PS phase of PVDF/PS blend. On the other hand, CNTs-PMMA tended to be localized in the interfacial regions of the blend, resulting in a lower electrical percolation threshold (0.07 vol%) when compared with nanocomposites produced with non-modified CNT (0.17 vol%). According to the authors, the PMMA chains grafted on CNT improved the compatibility of the carbon material with the PVDF
phase, explaining the selective CNT distribution in the interfacial regions of the PVDF/PS blend.

3 | CONCLUSIONS

The development and the use of different strategies to reduce the electrical percolation threshold content of polymeric antistatic packaging with carbon fillers as antistatic agents constitutes an important area of scientific research. The advances in nanotechnology, for example, have allowed the obtainment of new carbon nanomaterials with high electrical conductivity, as well as the production of hybrid polymeric nanocomposites by using carbon nanofillers with high and low AR, obtaining materials with low electrical percolation thresholds. Besides the AR, the particle size, and the electrical conductivity of the antistatic agents, other factors may affect the electrical percolation threshold content of polymeric antistatic packaging such as the compatibility between the composite phases, the crystallinity degree of the polymeric matrix, the processing route and the localization of fillers in multi-phase polymeric blends. The technological progress achieved has permitted the obtainment of advanced polymeric materials with promising electrical properties, low percolation thresholds, low costs, and great potential for use in the antistatic protection of electronic components.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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