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Smart Coatings with Carbon Nanoparticles

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Abstract

Smart coatings based on polymer matrix doped with carbon nanoparticles, such as carbon nanotubes or graphene, are being widely studied. The addition of carbon nanofillers into organic coatings usually enhances their performance, increasing their barrier properties, corrosion resistance, hardness, and wear strength. Moreover, the developed composites provide a new generation of protective organic coatings, being able to intelligently respond to damage or external stimuli. Carbon nanoparticles induce new functionalities to polymer coatings, most of them related to the higher electrical conductivity of nanocomposite due to the formation of percolation network. These coatings can be used as strain sensors and gauges, based on the variation of their electrical resistance (structural health monitoring, SHM). In addition, they act as self-heaters by the application of electrical voltage associated to resistive heating by Joule effect. This opens new potential applications, particularly deicing and defogging coatings. Superhydrophobic and self-cleaning coatings are inspired from lotus effect, designing micro- and nanoscaled hierarchical surfaces. Coatings with self-healable polymer matrix are able to repair surface damages. Other relevant smart capabilities of these new coatings are flame retardant, lubricating, stimuli-chromism, and antibacterial activity, among others.

Keywords: polymer nanocomposite, structural health monitoring, self-heating, self-healing, anti- and deicing

1. Introduction

Smart coatings are special covering materials which are able to sense and respond to an external stimulus. They are made with programmable materials, which respond to changes in light, chemical, thermal, or other stimuli. This brings them new performances, typically self-healing, self-cleaning, self-sensors, etc. due to their piezoelectric, thermoelectric, piezoresistive, and chemical properties (**Figure 1**). Most of the current smart coatings are based on nanoreinforced polymers. The incorporation of functional organic and inorganic nanofillers usually improves the thermal and mechanical properties of polymers, providing them new functionalities. As it is well-known, one of the main advantages to add nanofillers is their high specific area, which reduces significantly the nanofiller content and enhances the load transfer from the matrix, when the interface is suitable.

In this work, we focused on the addition of carbon nanoparticles, mainly graphene (G), graphene nanoplatelets (GNP), and carbon nanotubes (CNT). They
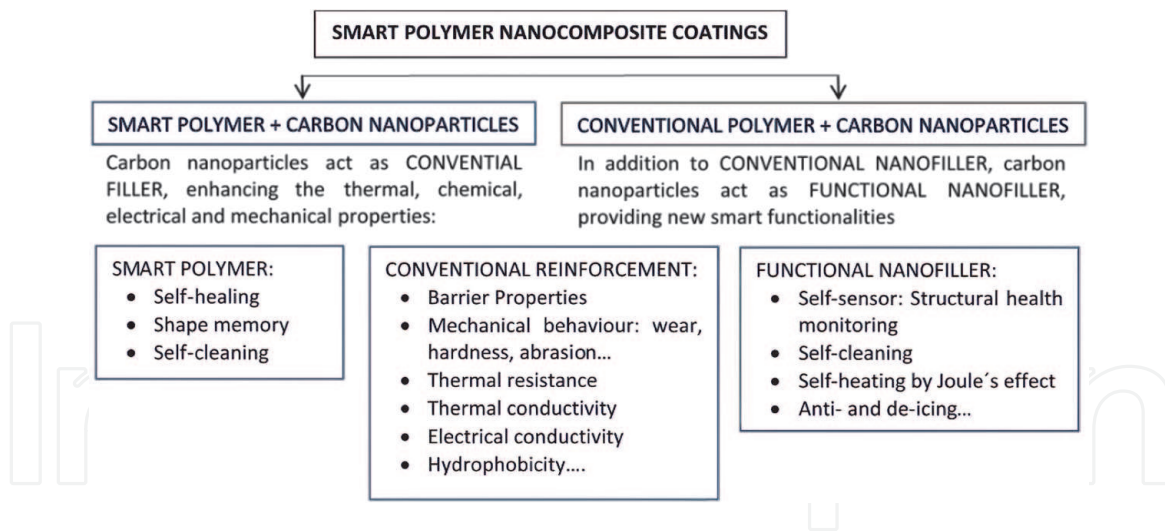
Figure 1.
Summary of smart coatings with carbon nanoparticles.

have extraordinary electrical and thermal conductivity and a unique combination of mechanical properties with great stiffness and high toughness [1–6]. They are composed of carbon, exhibiting low toxicity and environmental friendliness. For all these reasons, they are considered as multifunctional fillers of polymer matrix. In fact, polymer nanocomposites reinforced with carbon nanoparticles usually present enhanced mechanical, electrical, and thermal properties together with new performance as smart materials.

They can act as strain sensors due to their piezoresistive behavior, varying the electrical resistance of composite induced by the deformation of the electrical network formed by graphitic nanofillers. On the other hand, the nanofillers can be used as actuators, for example, as self-heater due to Joule's heating or as chemical absorbents. In this case, the matrix is a neat stimulus-responsive polymer, while the carbon nanofillers provide the stimuli to induce the polymer response.

2. Synthesis, processing, and main properties of polymer coatings

2.1 Synthesis and processing

The synthesis and processing of nanocomposite polymer coatings usually have at least two separated stages: the dispersion of nanofillers into the monomers, prepolymers, or polymers and the coating manufacture.

There are numerous different techniques to disperse the carbon nanofiller into monomers and polymers. In fact, there are numerous articles and reviews published. For this reason, in this chapter, they are only mentioned. It is well-known that the improvement of properties, in special mechanical ones, on nanocomposites is strongly dependent on the dispersion quality together with the polymer-nanofiller interface, which relies on the chemical and physical interaction between functionalized nanofillers and polymer matrix. Good dispersion of nanoparticles is critical to achieve high-performance nanocomposite. The most common **processing techniques of nanocomposites** can be organized on three ways: direct mixing, in situ polymerization in the presence of nanoparticles, and solution mixing. One more processing way is the in situ synthesis of particles, which is usually based on in situ sol–gel process inside polymers, but it is only used for inorganic nanofillers.

Carbon nanofillers must be dispersed on polymer or prepolymers depending on the polymer nature. The dispersion of nanofillers on thermoplastic polymers often carries out during the polymer manufacturing process, as extrusion or calandering. However, the nanofiller dispersion on rubber and thermosetting polymers is usually carried out in a previous step of curing process into monomers or prepolymers. In this last case, different dispersion techniques can be also applied, based on the application of mechanical forces or an electric or magnetic field.

As it was mentioned above, the second step consists on manufacturing the own coating, applying different common **processing techniques of coatings**. Cold spray process is commonly used for processing polymer nanocomposite coatings, avoiding the thermal deterioration of substrate. Dispersion, emulsion, and latex in situ polymerizations are other applied manufacturing processes.

2.2 Properties of nanocomposite polymer coatings

Graphitic nanofillers are often used to improve the **mechanical properties** of polymer coatings. The poor tribological performance of polymer coatings can be improved by adequately addition of graphitic nanofillers into the matrix because graphite is a solid lubricant. Polymer coating containing graphene can present excellent tribological properties, with low friction coefficient and reduced wear rate [7]. The increment of graphene content gradually decreases both friction coefficient and wear rate of composite coating. Under high temperature, graphene-reinforced thermosetting coatings show better friction reduction and wear resistance than neat coating. The values of these properties are enhanced by the increase of graphene content. Meanwhile, the friction coefficient and the wear rate of the graphene/composite coatings do not show a clear tendency with the increase of temperature. This behavior could be explained by the formation of a transfer film on the surface, which suppresses the huge heat and contact pressure [7]. CNT/polymer coatings can induce anti-friction, wear-proof, and self-lubrication performance [8], reducing the friction and improving the wear resistance. However, numerous factors affect their tribological behavior, such as the composition and properties of sliding pairs, such as their surface roughness and main mechanical properties (hardness, stiffness, and fracture toughness) and the sliding parameters, such as load, speed, temperature, and lubrication state, among others. This behavior is explained by the different involved mechanisms: bridge crack of CNT and lock the propagation of cracks, lubricant effect by dislodgement of individual graphene layers, strengthening of reinforced polymer matrix and dissipation of heat, and reducing the temperature induced wear [8]. It is worthy to note that there is an optimum carbon nanoparticle content to achieve the best tribological properties. However, this value depends on many factors such as aspect ratio of nanofiller, the dispersion degree and orientation of nanofillers, and the interactions with polymer matrix at interfaces.

The incorporation of carbon nanoparticles into polymer composites also increases their hardness. Increasing nanofiller content leads to improvement of hardness; however, the slope of the curve is reduced as the amount of graphitic nanofiller increases, which is attributed to agglomerations in the composite coating [9].

One of the most important applications of polymers reinforced with graphitic nanofillers is as **anticorrosive coatings**. The anticorrosive coatings can be classified in accordance to the protection mechanism against corrosion [10]: barrier protection, cathodic protection, anodic passivation, electrolytic inhibition, and active corrosion inhibition.

Graphitic nanoparticles enhances the **barrier properties** of polymer coating due to the "torturous path effect" and "nano-barrier wall effect," which strongly depends on exfoliation, dispersion, and orientation degree of nanofiller, their aspect ratio, the polymer-nanofiller interface, and the crystallinity of thermoplastic polymer or cross-linking degree of thermosetting resins. The presence of nanofillers constructs tortuous paths, decreasing the diffusion coefficient. The orientation of graphene and their high surface area forms a zigzag diffusion pathway hindering the diffusion of corrosion species. In addition, their excellent electrical conductivity prevents the electrons form the cathodic site by providing an alternative path [11]. The functionalization of graphitic nanofillers with polar groups [12] enhances the ionic resistance of coating by the creation of negative charge on the graphitic nanofillers surface when exposed to alkaline and neutral environment, preventing the diffusion of chlorine and hydroxyl anions.

In the last years, the development of **superhydrophobic** surfaces is being extensively researched. Superhydrophobic coatings have a wide range of applications in textile, automotive parts, construction, agriculture, optical, and maritime industry. It is well established that three factors are needed to create a superhydrophobic surface: low surface energy, microscaled roughness, and nano- and microscaled hierarchical surfaces [13]. The hierarchical multiscale surface can be achieved in coatings with high CNT content, forming CNT agglomerates at the microscale and CNT themselves at nanoscale. Polyvinylidine fluoride (PVDF) are commonly used as hydrophobic polymer coating. Water contact angle increases from 105° for neat PVDF to 170° with very high content of CNT [14]. Similar enhancement of hydrophobicity is reached by the addition of graphene nanoplatelets [15]. The superhydrophobicity is usually requested together with other functionalities, such as self-cleaning, anti-icing, and deicing, which will be addressed further on.

The incorporation of graphene into polymers allows increasing the **thermal stability** of polymer composite [16]. Higher specific area and aspect ratio of carbon nanofillers induce higher stability [17]. This enhancement is also accompanied with an important increase of the low thermal conductivity of polymers. Very high enhancements have been reported, from 0.2 W/mK for neat epoxy coating to 20 W/mK for composite with 30% graphene [16]. Graphene is more effective nanofiller than CNT in order to enhance the thermal conductivity of polymer composites. The thermal conductivity of graphene is attributed to phonons and electrons [18], justifying their excellent thermal conductivity (2000 W/mK). For example, copper is considered a good thermal conductor, whose conductivity is 400 W/mK. Here, the contribution of phonons is limited to 1–2% of total. The addition of nonfunctionalized graphene can induce an enhancement of 50% of thermal conductivity. However, when graphene is modified with functional groups, which is able to form covalent and non-covalent bonds with the polymer matrix, the increment can reach 100%. Moreover, a higher 300% of thermal conductivity increment is reached when graphene is modified with a titanium-coupling agent [19]. The researchers [18, 19] explained it by the reduction of interfacial thermal resistance between graphene and polymer due to the surface modification. For the same reason, higher dispersion degree of graphene into polymer matrix also enhances the thermal conductivity of composite.

It is well-known that the **electrical conductivity** is also increased by the addition of graphitic nanofillers. Higher specific area and higher aspect ratio of nanofillers decrease the nanoparticles which lead to reach an important enhancement of electrical conductivity, from 10^{-8} to 10^{10} S/m for the isolating polymers to 0.01–10 S/m for nanocomposites. Here, the functionalization of nanofillers usually implies a low enhancement of electrical conductivity of composites. This is

associated to the reduction of the electrical conductivity of neat nanofillers due to the partial breakage of some C-C structure during the functionalization and the surrounding isolating polymer layer formed over the functionalized nanofillers, which hinders the direct contacts between electrical nanoparticles.

Nanoreinforced coatings are being studied to improve the **flame retardancy** (FR) of flammable substrates [20]. The addition of graphene usually reduces the total heat release (THR) because they reduce the release of deleterious gas during thermal decomposition, arising from the radical trapping and layered hindering effect. CNT also enhances the FR behavior due to the strengthening of carbonized layers [21]. Also, they act as excellent physical barrier, reducing significantly the peak heat release rate (PHRR).

3. Smart nanocomposite coatings: Self-sensing

Among other functionalities, the concept of structural health monitoring (SHM) is of great interest in polymer coatings. It is based in an online inspection of the damage extent. In this context, a proper SHM technique must accomplish the following four levels, established by Rytter et al. [22]: (1) detection, (2) localization, (3) quantification of the damage, and (4) the estimation of remaining life, also known as *prognosis* (**Figure 2**).

Nowadays, there are a lot of different SHM techniques such as lamb waves, fiber optics, and acoustic emission, among others. However, they usually involve complex mathematical and statistical tools and do not often give an overall information of the health of the structure [23, 24]. Therefore, the development of SHM techniques is now gaining a great deal of attention.

3.1 Fundamentals of SHM with carbon nanoparticles

As commented before, carbon nanoparticles present unique mechanical and, especially, electrical properties in comparison to other materials [25]. Therefore, their addition into an insulating media promotes the creation of electrical networks. This fact induces an enhancement of the electrical conductivity of several orders of magnitude, becoming the polymer coating electrically conductive [26, 27].

Here, it is important, firstly, to define the concept of **percolation threshold**. It is the critical volume fraction of nanoparticles in which an efficient electrical network is formed, allowing the current flow. It depends on several factors mainly related to the geometry of the nanofiller (including their 0D, 1D, or 2D nature) as well as their dispersion state, that is, their distribution inside the nanocomposite. The determination of the percolation threshold is a crucial factor that determines the minimum content of nanofiller that is needed for electrical applications.

Furthermore, the influence of the different parameters of the nanoparticle network in the percolation threshold has been widely studied in the last years. Li et al. [28] proposed a simple analytical model correlating the geometry, aspect ratio, and
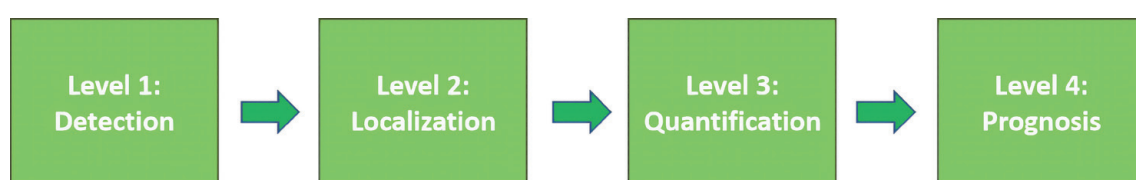
Level 1: Detection → **Level 2: Localization** → **Level 3: Quantification** → **Level 4: Prognosis**

Figure 2.
Schematics of the four SHM levels established by Rytter et al.

dispersion state with the value of the percolation threshold. They concluded that the lower the aspect ratio and the higher the degree of agglomeration of nanoparticles, the higher the percolation threshold. In this context, carbon black (CB) reinforced polymers show very high values of percolation threshold [29] due to their low aspect ratio Bauhofer et al. [30] did an extensive review of percolation threshold in carbon nanotube (CNT)-based polymer nanocomposites by analyzing the effect of nanofiller geometry and dispersion technique. It was observed that the most aggressive dispersion procedures, such as ultrasonication, although leading to the most homogeneous distribution of nanoparticles, lead to a very significant breakage of the CNTs. This prevalent reduction of the aspect ratio leads to increasing values of percolation threshold.

However, the effect of dispersion procedure varies depending on the nanofiller. In this case, ultrasonication has proved to be a good dispersion technique for graphene nanoplatelet (GNP)-based nanocomposites. GNPs are formed by several layers of graphene, and it is widely used as reinforcement in polymer nanocomposites because of the lower cost. Here, ultrasonication promotes the exfoliation of the graphene layers [31]. Therefore, these exfoliating mechanisms induce a reduction of the percolation threshold due to an increase of the aspect ratio of the nanofillers. The combination of an ultrasonication stage with three roll milling can promote the creation of GNP nanocomposites with very low percolation threshold due to the combination of exfoliation stretching effects.

The concept of SHM with nanoparticles, therefore, is based in the monitoring of the changes of the electrical network when subjected to strain or damage. However, for a better understanding of these SHM techniques, it is important to know which are the main conducting mechanisms in the electrical network. Here, three different mechanisms can be identified: the intrinsic conductivity of the nanofiller, the contact between adjacent nanoparticles, and the tunneling transport that takes places between two neighboring particles that are not in intimate contact. Among them, the tunneling transport plays a dominant role in the electrical network of the nanocomposite [32]. It is explained because the associated tunneling resistance is several orders of magnitude higher than the intrinsic and contact resistance. Therefore, the variations of the electrical network when subjected to strain or damage will be ruled by the variation of the tunneling distance between nanoparticles.

In this regard, Simmons [33] established a linear-exponential correlation between the tunneling resistance and the interparticle distance, also known as tunneling distance. It means that the higher the separation between neighboring nanoparticles, the higher the electrical resistance is. More specifically, when subjected to strain, there is a variation of the electrical resistance that is correlated to an increase of the tunneling distance between adjacent nanoparticles:

$$R_{tunnel} = \frac{h^2 t}{A e^2 \sqrt{2m\varphi}} \, exp \left(\frac{4\pi t}{h} \sqrt{2m\Phi} \right) \qquad (1)$$

where R_{tunnel} is the tunneling resistance; t is the tunneling distance; h is the Planck's constant; m and e are the electron mass and charge; A is the area in which electrical transport takes places or tunneling area; and φ is the height barrier of the matrix.

3.2 Sensitivity of polymer-based nanocomposites

In this context, the concept of percolation threshold that has been discussed before plays a key role. In fact, the linear-exponential dependence means that the

higher the tunneling distance at the initial situation, that is, when no strain is applied, the higher will be the electrical resistance variation associated to the variation in the tunneling distance when applying strain, as can be observed in **Figure 3**.

Here, it is necessary to define the concept of gauge factor (GF), as the variation of the normalized resistance $\Delta R / R_0$ divided by the applied strain, ε:

$$GF = \frac{\Delta R / R_0}{\varepsilon} \qquad (2)$$

Therefore, in order to achieve the highest GFs, it would be necessary to work with volume fractions of nanofiller near the percolation threshold, as the distance between adjacent nanoparticles will be the highest possible to form an efficient electrical network and, thus, the variation of the tunneling distance will be the highest. This has been observed in both GNP and CNT nanocomposites, where the contents near the percolation threshold achieved the highest GFs [34, 35].

However, in this sense, there are significant differences among the different nanoparticles. For example, GNP-based nanocomposites have shown a more accused exponential behavior of the electrical resistance with applied strain [35] than CNT-based ones [36]. It means that the values of GF at low strain levels are much lower than at high strain levels.

This accused exponential behavior of GNP nanocomposites can be explained accordingly to the different interactions that take place inside the electrical network. In fact, the tunneling area of these 2D particles is, generally, much higher than in the case of CNTs, and it leads to the fact that the value of the interparticle distance can be much higher for an efficient tunneling transport. Therefore, as explained before, the higher the tunneling distance, the more accused the exponential correlation between the electrical resistance and the applied strain will be.

Moreover, there is also a correlation between the exponential behavior and the sensitivity of the nanocomposite, and, thus, GNP-based ones show higher GF values than CNT nanocomposites (from 12–15 to 2–4 at low strain levels, respectively, for nanocomposites manufactured following similar techniques) [35, 36].
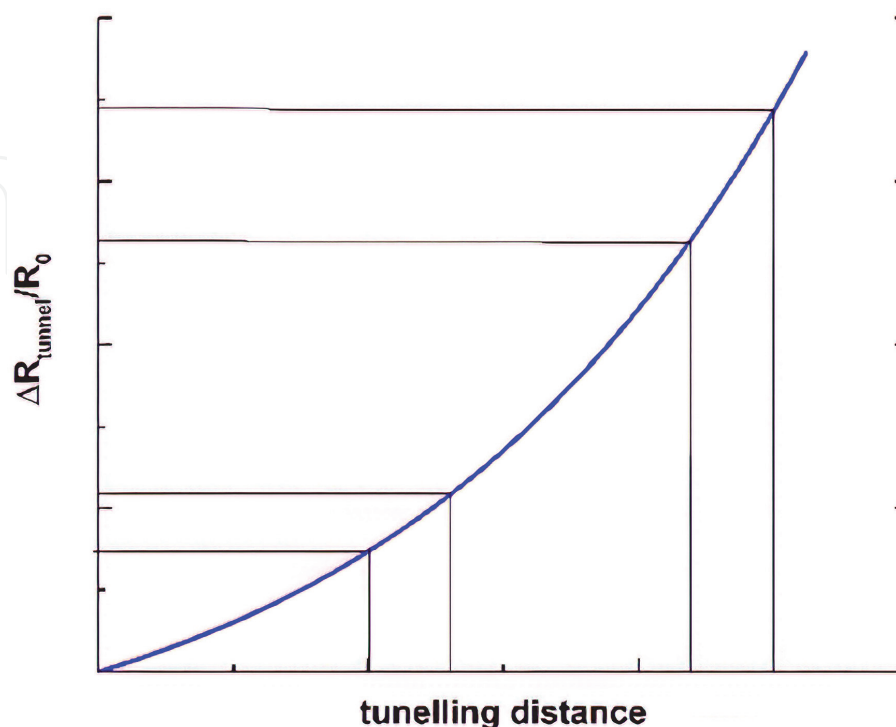

Figure 3.
Variation of the tunneling resistance as a function of the tunneling distance between nanofillers.

3.3 SHM in nanocomposite coatings

The enormous potential of the nanoparticles for SHM applications has been widely exploited in the development of surface sensors and smart coatings. More specifically, their use as substitutes of strain gages is gaining attention nowadays.

Basically, a strain gauge is a device for indicating the strain level of a structure at the point of attachment. To date, the most used are based in conventional metallic foils in which the strain is obtained from the electrical resistance variation due to the deformation of the metallic foil when subjected to this strain level. GF values of conventional strain gauges are around 2 and usually show a very linear dependence of electrical resistance change with applied strain.

The research in strain-sensing devices with carbon-based nanocomposites is mainly focused in the development of highly stretchable sensors. In this regard, graphene, carbon nanotubes, and other carbon nanoparticles, such as carbon black, have been widely explored, among others. The addition of these nanoparticles to polymers with high strain capabilities such as fluoroelastomers [37], thermoplastic polyurethane [38], or vulcanized silicone [39] has demonstrated excellent sensing capabilities. More specifically, they present enormous potential for human motion sensing or wearable electronics [37] as the GF at high strain levels (>20%) can be in the range of 400–4000 depending on the content and morphology of the carbon nanofiller. Here, a highly accused exponential behavior is observed at higher strain levels due to the prevalence of tunneling mechanisms in the carbon nanoparticle network. In addition, they can be also used as pressure sensors, with excellent sensing capabilities in comparison to others [40] as they are able to detect very small pressure changes due to the strain induced fail that they promote.

Here, it can be stated that the 2D nature of the electrical network in a nanocomposite coating promotes an increase of the percolation threshold when compared to a bulk nanocomposites, where a 3D uniform disposition of the nanofillers is supposed to be [41]. Moreover, the cross-sectional area of the coatings is obviously much lower than 3D nanocomposites, so the electrical resistance is
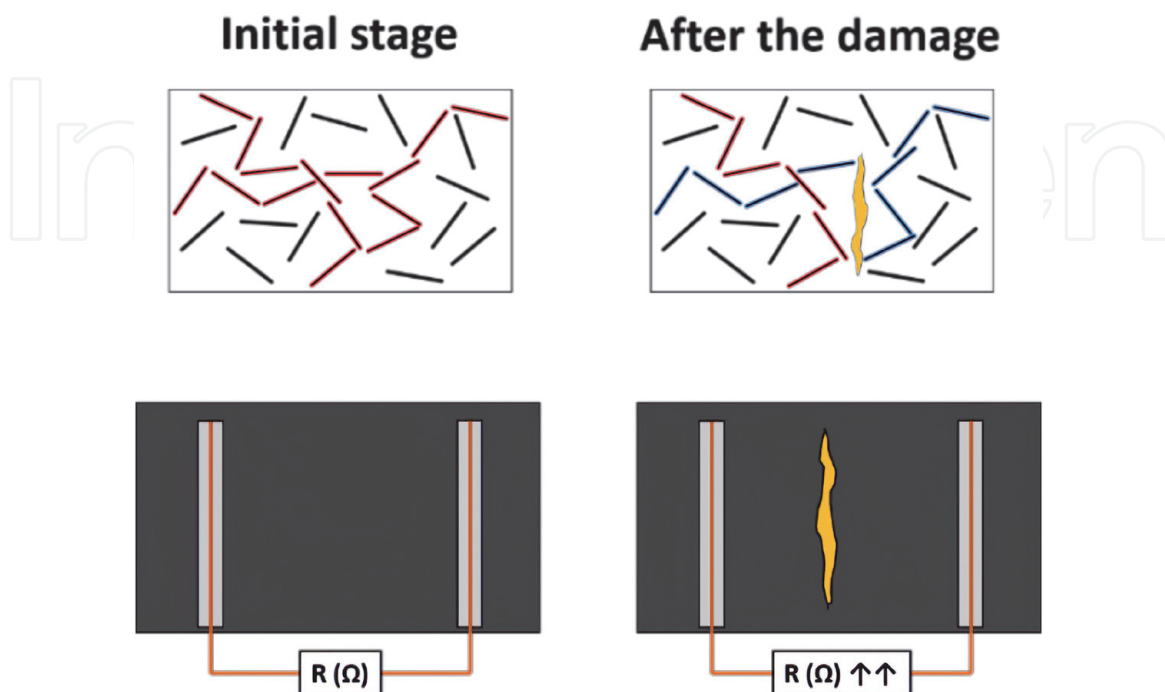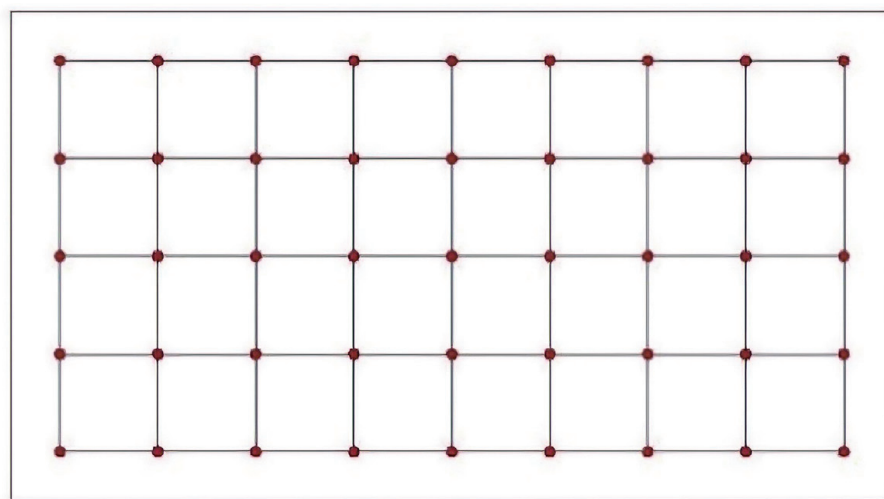

Figure 4.
Schematics of the effect of a crack in the electrical network.

much higher. Therefore, the amount of nanofiller necessary for SHM purposes is much higher in polymer coatings.

Furthermore, apart from flexible devices such as strain gauges, wearable electronics, or human motion sensors, their SHM capabilities in other polymer coating based on thermosetting polymers have been widely demonstrated. More specifically, GNP-based coatings have proved to be very sensitive at low strain levels to both tensile and compressive loading, as well as a good repeatability under cyclic loads [42]. In addition, CNT-based ones have also demonstrated good sensing properties with a high linearity [43].

Although the interest as strain sensing devices is very significant, their crack sensing capabilities can be even of more interest. Here, the crack detection is based in a sudden breakage of the electrical pathways due to the presence of the crack itself. It will be reflected in a sharp increase of the electrical resistivity of the coating, and, thus, the electrical resistance during the measurement will increase as well, as shown in the schematics of **Figure 4**.

In this regard, electrical impedance tomography is gaining a great deal of attention as an SHM technique. It is based in a mapping of the electrical conductivity of a structure based in the electrical resistance measurements on its surface. Therefore, by using this technique, it will be possible to detect, locate, and even quantify

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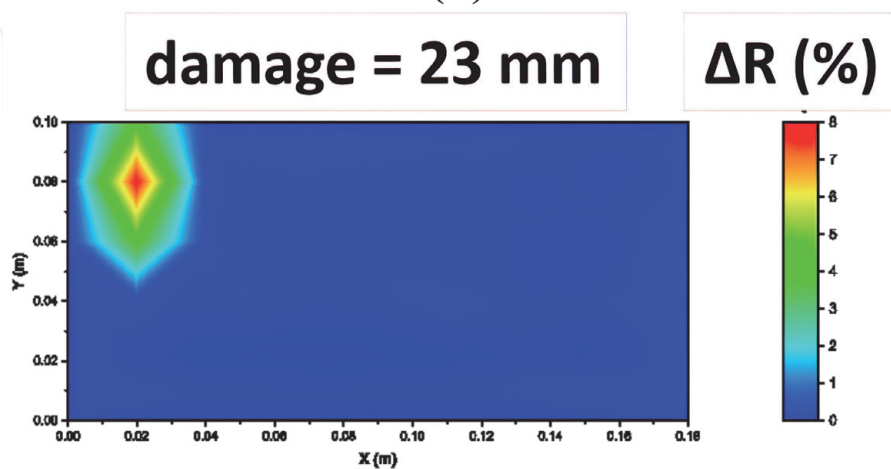
(b)

Figure 5.
(a) Schematics of electrode disposition and (b) mapping of variation of the electrical resistance correlated to an induced damage [43].

superficial defects by analyzing the changes of its surface resistivity. In this context, their effectiveness has been widely demonstrated in polymer coatings for the detection of superficial cracks [43], where the electrical resistance measurement between adjacent channels can easily detect an artificial damage (**Figure 5**), as well as in sensing skins for spatial pressure mapping, where the strain induced by the applied pressure is monitored [44]. Here, the main issue is correlated to the positioning of the electrodes and the data processing, which usually involves the use of complex mathematical tools. However, the results for SHM applications are very promising and give a new functionality to nanoreinforced polymer coatings.

4. Smart nanocomposite coatings: Self-heating

Surface heating is a challenge for several applications, and it is usually carried out by different approaches such as external heating source (portable equipment) or heating elements positioned on the surface (i.e., electrical resistances) which, in fact, modifies the surface quality of the parts where they are positioned. Heat is required in organic coatings for different purposes:

- Deicing systems: ice accretion to surfaces when subjected to cold and humid environments is something very common that requires the use of deicing alternatives, and, among them, heat of the surface to create a liquid film can be of great interest.

- Self-curing coatings: the use of coatings with curing temperatures above 23°C is often limited because of the need of external heating sources that makes the production more difficult. Nevertheless, the glass transition temperatures or hardness are usually higher for higher cross-linked coating, thus making more interesting the use of higher curing/post-curing temperatures.

- Heat activated self-healing mechanisms: as previously mentioned, the main source for self-healing activation is UV radiation and temperature. Nevertheless, the requirement of a heating source limits the application of these promising coatings to structures with easy access to be heated.

These applications will be further explored after an explanation of basic aspects of self-heating coatings based on the introduction of conductive nanoparticles inside polymer matrices, such as CNTs and GNPs. Nevertheless, these types of coatings are not limited to these applications, and they can find a potential field to be implemented in any product that need to be heated such as heating seats for commercial vehicles [45], floor heating, heating textiles, etc. where temperatures required are usually below 100°C [46].

4.1 Fundamentals of self-heating by Joule effect

The addition of carbon nanoparticles inside a polymer matrix above the percolation threshold, which has been previously explained, allows getting an electrically conductive material. The electrical current that flows through the material will generate heat according to Joule's law (Eq. (1)), which is commonly known as Joule effect in materials:

$$Q = i^2 R t \qquad (3)$$

where Q is the heat generated, i is the current flow, R is the electrical resistance, and t is the time the current is applied.

The first thing that can be analyzed from Eq. (1) is that higher current intensity would lead to higher heat generated and, consequently, higher contents of carbon nanoparticles will be desired for this purpose in order to increase the temperature reached or to reduce the voltage required. Although all common carbon nanostructures can be used for this purpose (carbon black, carbon nanotubes, graphene nanoplatelets, or even graphite flakes), the importance of reaching high intensity values usually gives the best results for CNT-filled materials [47]. In fact, very high CNT amounts can be found in the literature in order to increase the electrical conductivity and, consequently, the current flowing at lower voltages applied. This is the case of the study based on ABS as matrix where CNT was added up to 15 wt.% in order to allow reaching temperatures over 200°C when voltages of only 12 V were applied [48] or the research carried out by Chu et al. where similar results in terms of temperature and voltage at contents of 7.5 wt.% of CNT in PDMS were found [49]. The interest in the use of low voltages is based on the use of batteries commonly installed in cars and trucks, among others.

Apart from the heat generated, there is an important fact regarding these percolated electrically conductive networks, which is the homogeneous distribution of heat through the coating. Two important effects must be taken into account for this aspect: (1) thermal conductivity of polymers which is particularly low, thus making heat transfer through the coating more difficult, and (2) homogeneous presence of the carbon nanoparticles through the polymer matrix, which is not always easily reached.

Both CNTs and GNPs show extremely good thermal conductivity individually. Nevertheless, in spite of their similar intrinsic thermal conductivity, the morphology of GNPs makes them more interesting for this purpose, even when compared to SWCNT [50]. Even at the same content of both types of nanoparticles, Zakaria et al. found that the thermal conductivity was higher for GNP nanocomposites than the MWCNT ones. In fact, although for electrical properties, higher contents of GNPs are usually required to meet similar properties to the ones found for MWCNT, in that case, at only 3 wt.% of nanoreinforcement, GNP nanocomposites showed an increase of 126.4% in thermal conductivity while 3 wt.% of MWCNT only increased this property by 60.2% [51]. In fact, experimental values of thermal conductivity are usually lower than those predicted theoretically, and it has been attributed mainly to waviness, dispersion, alignment, interfacial resistance, and contact resistance [52].

Proper exfoliation of GNPs causes an important increment on thermal conductivity related to an increase of the aspect ratio. Chu et al. [53] proposed a model to calculate the thermal conductivity of nanocomposites based on randomly oriented nanoparticles which takes into account geometrical aspects of the nanoparticles (aspect ratio) as well as differences in the intrinsic thermal conductivity of the nanofiller in each direction. In the case of GNPs, these aspects will be strongly related to their exfoliation and dispersion in the polymer matrix. On the other hand, the waviness of the nanoreinforcement may reduce the effective aspect ratio of the nanofillers which lead to propose few layers GNPs as an optimal solution instead of individual monolayers that tend to roll up easier during dispersion stage.

These self-heating coatings do not require extremely high thermal conductivities, but they should be high enough to ensure good heat transfer through the whole surface for the purposes mentioned above.

The formation of aggregates is very common in this type of materials, and this may cause that at very low carbon nanoparticle loadings, some resin areas are free of nanoreinforcement, which leads to nonuniform heating of the samples. In that
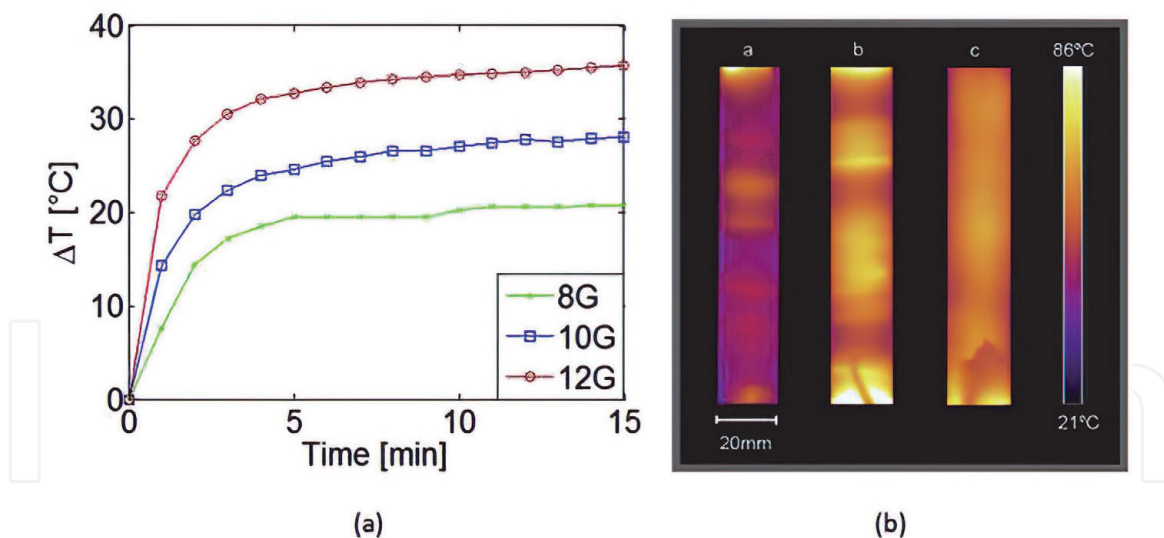
Figure 6.
Joule effect heating of epoxy nanocomposites containing (a) 8 wt.%, (b) 10 wt.%, and (c) 12 wt.% of GNPs [54].

cases, the thermal conductivity of the sample is even more important, as heat will not be homogeneously generated, thus making more important its thermal conduction. Prolongo et al. showed this effect when comparing MWCNT loaded with GNP ones, and they found that differences between maximum and minimum temperatures were much higher in those specimens based on MWCNT [47]. When adding GNPs, also this effect was found as lower contents of GNPs lead to areas with lower nanoreinforcement concentration, thus leading to higher temperature differences between different areas in the same sample, while the samples containing higher GNP contents (12 wt.%) showed more uniform heating (**Figure 6**).

4.2 Self-heating as deicing system

Icing on structure surface can seriously affect the function of the system, and, even, it may cause its damage and consequently the need for replacement which leads to economic, environmental, and security issues. Wind turbines or aircraft surfaces are examples in which ice accretion has a detrimental effect on operation conditions by modifying the aerodynamic profile, structural weight, etc. [55, 56]. Most strategies currently used are based on two different approaches that affect the coatings used:

- Passive methods which do not require external energy source. The main advantage of these methods is their lack of energy consumption to operate; nevertheless, their effectiveness is usually lower, so they are commonly used in combination with active methods to reduce the power needed [57]. Hydrophobic coatings are one of the passive methods most widely accepted which can be achieved by different approaches such as the addition of nanoparticles or tuning of surface textures in multiple length scales based, among others, in biomimetic techniques [58, 59]. This aspect has been discussed in Section 2.2.

- Active methods which require external energy source. These methods are usually more effective to avoid icing problem and can be used in combination with passive methods. Among these active methods, heating systems are the most reliable ones in spite of the power consumption although mechanical ice breakage by means of inflatable rubber boots can be found in small airplanes. When heating the surface, several approaches can be used (infrared heating and warm air conduction, among others), but electrical resistance heating

seems to be one of the most promising ones. To avoid the use of additional membranes or layers, multifunctional coatings with heating capability by thermoresistive methods at the same time they protect the underlying structural material are very interesting.

The use of carbon nanostructures has been studied for this purpose trying to create an active method based on Joule effect heating at the same time that hydrophobicity is increased by the addition of these nanoreinforcements. With this purpose, several research efforts have been already done reaching very promising results in terms of temperature, homogeneity, heat rate, and power consumption. By the use of GNPs, Redondo et al. achieved 35°C of temperature increments at 800 V with a heat rate of 13.6°C/min and a power consumption of less than 3 W. This temperature increment should be enough to produce ice melting on the coating and, consequently, separation of the ice accreted to the surface, even at severe ambient temperatures below −20°C [54]. When using CNTs, the electrical conductivity of the materials is usually higher than GNPs, thus increasing the value of the intensity at a constant voltage which is useful for heat generation according to Eq. (1). CNT/PVA films with very high CNT concentration have been produced in order to get very low electrical resistance and, consequently, higher electroresistive heating. The same procedure, using high MWCNT loadings (10 wt.% in poly-1,3,4-oxadiazole), allowed to reach temperatures above 100°C by the application of only 40 V in these nanoreinforced films. Prolongo et al. compared the temperature reached by the use of CNTs and GNPs as nanoreinforcements, and with contents of 0.5 wt.% of CNTs, the temperature reached almost 100°C with only 90 V applied, while 300 V were required to go over 65°C when 8% GNP were added [47]. Nevertheless, the authors claimed that temperature was more homogeneous when GNPs were used as nanoreinforcement.

Finally, the authors are currently exploring the possibility of using the electrical network of CNTs to sense the temperature and, consequently, activate the voltage application when required because of the weather conditions measured by the coating itself. Coatings based on CNT/PDMS were manufactured and showed an effect-denominated negative temperature coefficient (NTC). This effect on electrical response was nonlinear with temperature changes, being the sensitivity more than six times higher in the range −5 to 5°C than at room temperature, which makes them potential candidates for temperature measurement for smart coatings being able to detect temperature and activate the voltage required accordingly [60].

4.3 Self-curing coatings

Based on the same basics of previous applications, self-heating nanoreinforced polymers have been developed in order to allow curing by electrical voltage application. This issue has been already explored to take advantage of the uniform heat as far as the heat is generated from the material itself and, also, of the absence of power loses associated to heat transmission from the heating element to the material itself, as it happens when ovens are used [61]. Mas et al. proved the efficiency of this curing method by the addition of MWCNT to an epoxy matrix, and they found uniform thermal properties in the resin cured by Joule heating. In fact, they were able to control the real curing temperature by the coupling of thermocouples to the voltage source with a PID controller. The input of the thermocouples was used by the PID to adjust the power supply in order to keep the curing temperature constant during the process. One of the main advantages they found was the high heating rate as the heat emerges from the material itself.

This fact was also proved by Jang et al. in the research conducted to prove that curing by Joule heating of thin films of PDMS reinforced with high loadings of

CNT (7 wt.%) could lead to even better performance than the equivalent oven-cured samples. They measured the mechanical properties of both materials, and they found that stiffness of samples cured by Joule effect heating was slightly higher, which was associated to faster and more uniform heating of the whole material volume. So they conclude that this curing technique could allow obtaining materials at shorter curing times, more homogenous, and with higher cross-linked structures [62].

Other carbon nanostructures different from CNTs have been also studied to cure thermoset materials out of the oven, such as the previously study from Mas et al. established [61]. Xia et al. proposed the use of GNP to cure epoxy matrices by adding contents over 8.5 wt.% as they found this value to be the percolation threshold for the GNP morphology and dispersion technique used. They found curing degrees similar to those found for oven-cured samples but with much faster heating rates and more homogenous curing, similar to the studies previously mentioned. Nevertheless, they found preferential orientation of the GNPs which was associated to the presence of an electric field during curing stage as it was not observed in oven-cured samples. This fact is very important as they found improved electrical and mechanical performance in this direction, but this aniso-tropic behavior must be taken into account when designing elements with these materials [63].

So, the application of curing by Joule effect heating has been proved as possible in electrically conductive networks based on carbon nanoparticles inside polymer matrices with particular interest due to faster curing cycles, more uniform curing degree, and easy application in large structures/surfaces.

4.4 Self-healing coatings

Any thermally activated mechanism could be beneficiated from the previously explained self-heating by thermoresistive heating. Thermo-reversible Diels-Alder reactions are one of these examples, in which the Diels-Alders and retro-Diels-Alder reactions are favored at different temperatures allowing the restoration of the covalent bonds, thus repairing the cracks generated. This method was used by Willocq et al. to produce MWCNT nanoreinforced polymer matrices with self-healing capabilities by Joule effect heating at low voltages of 25 V which were enough to reach the retro-Diels-Alder reaction temperature in the vicinity of the macroscopic damage (crack) due to local higher heating around the crack. This local temperature increment around the crack was strongly dependent on the position of the electrodes with respect to the direction of the crack [64].

Huang et al. used GNPs dispersed in a thermoplastic polyurethane (TPU) matrix in order to create a percolated network and reach 98% self-healing efficiency by the application of 220 V to the material. The use of GNPs in this case allowed improving alternative self-healing approaches such as heating by IR radiation absorption which is also enhanced by the presence of GNPs in the matrix, thus allowing different alternatives to improve the thermal self-healing process of the TPU [65].

Also, this Joule effect-based heating can be used to activate self-healing in thermosetting/thermoplastic blends which self-healing capabilities. This mecha-nism is activated by a temperature increase above the melting temperature of the thermoplastic material used and high enough to allow its proper flow through the cracks created. Several materials have been studied for this purpose, and, among them, polycaprolactone (PCL) has been widely studied due to its low melting temperature which can allow self-healing mechanism to take place at temperatures around 100°C to allow its proper flow [66]. Zhang et al. proved the efficiency of the addition of CNT to EVA/PCL composites with shape memory purposes, which

allowed heating the blends up to 100°C which would be enough to activate self-healing mechanisms in blends containing PCL as healing phase [67]. All these recent studies reveal that the use of self-heating can help to develop self-healing polymer-based materials with the main advantages to avoid the use of external heat sources, use electrical voltage that could be remotely activated, allow heat to emerge from the material itself avoiding heating other materials parts, and reduce losses due to heat transfer.

5. Smart nanocomposite coatings: Self-cleaning

Self-cleaning is a surface property consisting in keeping the surface clean under severe environmental conditions [68]. It is inspired from lotus effect with a specific micro- and nano-hierarchical surface morphology and low surface energy, providing superhydrophobicity. A surface can be considered as superhydrophobic when the water contact angle is higher than 150° (WCA > 150°) and the low sliding angle is lower than 10° (SA < 10°). Another opposite approach for getting self-cleaning surfaces is the incorporation of photocatalytic fillers affording hydrophilic surfaces (WCA < 5–10°) able to keep free of organic contaminants and moisture. The self-cleaning surfaces can be developed with nanodoped polymer coatings and with neat graphitic coating, such as it is shown in **Figure 7**.

One of the most studied self-cleaning materials is based on titanium oxide (TiO_2) and zinc oxide (ZnO) due to their superhydrophobicity and photocatalytic decomposition ability of organic pollutants. These coatings are usually manufactured by sol-gel process. Modifying these nanofillers with graphene or its derivatives can enhance their visible light response. Hybrid TiO_2/graphene nanofillers can exhibit strong electronic overlap and high interfacial binding energy; thus, photoexcited carriers can transfer from TiO_2 to graphene, and its band gap is reduced, improving the visible light photoresponse [69, 70]. Nevertheless, graphene enhances the photocatalytic efficiency of ZnO due to that graphene accepts the electron from ZnO nanoparticles, preventing the recombination of photo-generated electron hole in the semiconductor. These nanocoatings show superhydrophobicity when they are irradiated with visible light. An interesting alternative approach is the impregnation of cotton fibers to manufacture industrial self-cleaning textiles [71]. The treated fabrics exhibit an increase anti-bacteriological behavior and high biocompatibility.

Another possibility to develop superhydrophobic self-cleaning coatings is the use of hydrophobic polymer matrix, such as polysiloxanes or fluoro-polymers,
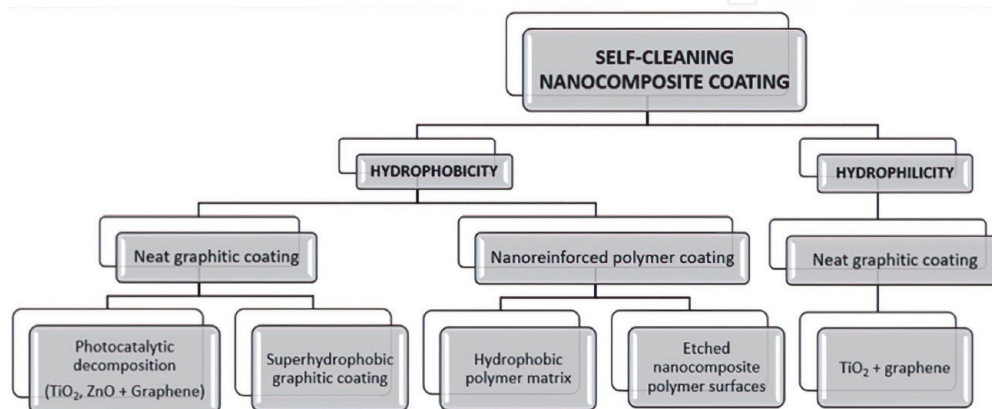

Figure 7.
Scheme of the main approaches of self-cleaning coatings with carbon nanoparticles.

doped with graphitic nanofillers, giving high electrical conductivity [72]. These coatings present high water contact angle and low sliding angle. In addition, they exhibit high wear resistance and excellent anticorrosion performance [73]. The presence of polymer matrix enhances the adherence with substrate and increases the chemical resistance. When the matrix is not hydrophobic polymer, the nanocomposite coating can be chemically etched (i.e., fatty acids such as stearic acid, palmitic acid, and oleic acid) in order to decrease the surface energy. This approach allows using very different matrices (i.e., acrylic resin, epoxy, etc.), looking for other advantages, such as superior adhesion, mechanical properties, low cost, etc., making it suitable for many industrial fields. Together with self-cleaning behavior, other related properties are commonly developed in smart coating based on carbon nanoparticles, such as antifouling, antimicrobial, anticorrosion, anti-soiling, etc. Graphetic nanostructures hold antimicrobial and antibiofilm activities, although the involved mechanisms are not completely understood and accepted [74]. For these applications, other nanoparticles of gold, silver, copper, TiO_2, ZnO, Fe_2O_3, and CuS, are anchored to the graphene nanosheets to enhance the bactericidal efficiency. Now, current efforts consist on developing membranes and films with polymer matrix, such as chitosan, poly(vinyl alcohol), polyamides, polyethyleneimine, etc., for applications in disinfection, gas separation, and water desalination.

6. Conclusions

The development of polymer coatings with carbon nanoparticles is now gaining a lot of interest. They present enhanced electrical, thermal, and mechanical properties that can be used to confer new functionalities, turning into smart materials, able to interact with the environment, responding appropriately to external stimuli. These new functionalities are possible thanks to the creation of an effective electrical, thermal, or mechanical network inside the polymer matrix, making it possible for their use for structural health monitoring applications, resistive heating by Joule's effect among others such us self-cleaning and self-healing.

Acknowledgements

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