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Chapter

Novel PTC Composites for Temperature Sensors (and Related Applications)

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Abstract

This chapter presents a brief description of conductive polymer composites in general, with more attention paid to those exhibiting abrupt change of resistivity when temperature raises, associated with PTC and NTC (respectively, positive and negative temperature coefficient of resistivity) effects. These materials are "smart" because they can adapt their electrical behavior to environmental characteristics, hence being suitable for temperature sensors, smart heating devices, safe batteries, and resettable fuses. As compared to NTC, the applications of PTC materials are more numerous, because the abrupt increase of resistivity with temperature rise allows the current and temperature to be naturally limited. The PTC effect and the factors controlling its quality, e.g., repeatability, intensity, switching temperature, and sub-sequent NTC effect, are discussed from the point of view of the influence of the nature of polymeric matrix, conductive fillers, and applied treatments. Increased attention is paid to composites with conductive carbonaceous fillers, and these materials being of great interest because they have considerably lower density than metals, are easier to process, and can impart surprising mechanical and electrical properties to polymer matrices. Examples and applications of temperature sensors based on PTC composite materials, applications, and perspective aspects are discussed within the chapter.

Keywords: temperature sensors, thermistor, positive temperature coefficient, conductive polymer composites, carbonaceous materials

1. Introduction

A sensor is a device that responds to a chemical or physical stimulus by generating a signal that can be analyzed electronically. In general, to be suitable, sensors and devices incorporating them must have a fast response to external stimulus, be able to detect fine variations in the analyte, have a low recovery time, identify the desired analyte among other stimuli, and be a reliable tool, easy to operate, preferable also in *in situ* measurements [1]. In addition, it is desirable to have a low cost and environmental compatibility. Although there are a large number of sensors proposed in the literature, continuous concerns for the improvement of sensors are justified by the need to improve existing systems as well as to find new promising alternatives that

allow the change of old analysis and measurement technologies. A widely investigated possibility in the last decades is the use of nanomaterials, a category that seems to offer an infinite practical field of solutions for the most diverse problems. Among the various nanomaterials, nanostructured carbonaceous materials show numerous advantages compared to other materials due to their specific properties as well as convenient costs, which make them suitable for use as technological sensors. Therefore, special attention will be paid in this chapter to recent advances in the field of resistive temperature sensors using such materials.

Temperature sensors are indispensable in various fields of engineering (electrical, automotive, aerospace, communications, civil engineering [2], health care, human machine interface, robotics, etc. [3]). Therefore, among the sensing technologies, the temperature sensor is probably the most widely used. The signal given by resistive temperature sensors consists of the increase or decrease of resistivity or capacitance with temperature [2]. The continuous improvement of the performance and manufacturing processes of sensors in general and of temperature in the present case, as well as the expansion of application fields, are current concerns of materials science and related disciplines.

Among the directions of perspective or current interest for thermal or multifunctional sensors that include temperature detection are flexible electronics [2] for intelligent house applications (e.g., electronic wallpaper, an interactive system that incorporates a network of sensor temperature and an air conditioning control system [4]), robotics (humanoid artificial skin [5, 6]), control of working conditions in mechanical or electronic systems, instruments wearables for physiological monitoring, smart packaging that indicates the state of freshness of food, etc. [6, 7]. In such applications, portable temperature sensors, flexible themselves, capable of detecting several signals simultaneously (temperature, pressure, and strain), the so-called multifunctional sensors (or physical sensors) are often required, or, on the contrary, the temperature signal should not be affected by the action of other factors, such as mechanical deformation (monofunctional sensors, in our case, temperature sensors) [7]. Some of the portable, flexible sensors proposed in recent years are PTC resistive sensors [6, 7].

A major obstacle to the practical realization of stretchable resistive temperature sensors from composite materials is the limited ability of the conductive phase to be stretchable during use, that is, to retain its sensitivity unchanged to repeated, large-amplitude deformations. Obviously, work must be done on the conductive phase, by finding conductive nanoparticles, capable of favorable interactions with the macromolecular chains of an optimally chosen elastomeric matrix. For this purpose, metal nanoparticles, carbon nanotubes (CNTs), graphene, as well as different preparation techniques, have been tested. The polymer substrates used for flexible printed sensors are mainly polymers containing aromatic rings in their structure, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyimide (PI), which are available as films with large surface areas, at reasonable prices, allowing the obtaining of reasonable production costs [8].

Stretchable (elastic) temperature sensors are usable in a wide range of applications, such as wearable real-time health care devices, monitoring working conditions in mechanical or electronic devices, wearable instruments for physiological monitoring, and smart packaging. Their realization involves the use of matrices or elastic supports. Temperature sensors often need to accompany stretchable strain sensors in applications such as wearables for recording human physical movements, therapy devices, and health monitoring such as heart rate monitoring [2]. Extensible strain and

temperature sensors are also required for measuring deformations on extensible and curved surfaces (deformation of the skin on the wrist, e.g.) or for measuring the stress developed on the curved surfaces of pressure vessels, often requiring that local temperature information to accompany the strain information.

The properties of conductive polymer composites (CPCs) as temperature sensors have been reviewed in various previous works [9–12].

This chapter is dedicated to the recent progress made in the field of temperature sensors with PTC properties and their applications, which tries to develop and complement the previous information, aiming also to give an overview of the subject. Although not the subject of this chapter, some notable examples of NTC sensors are also included.

2. Conductive polymer composites. PTC effect

Unlike intrinsically conductive polymers (see [13–15], such as polyacetylene, polyaniline (PANI), polythiophene, polypyrrole (PPy), poly(p-phenylene vinylene), or PEDOT:PSS), the polymer composites, consisting of an electrically insulating polymer and a conductive phase, are much easier to prepare and have high chemical stability, and their electrical conductivity can be varied simply, within very wide limits, by changing the nature and the concentration of the conductive filler, changing the nature of the polymers used as a matrix, as well as by changing some technological factors (such as mixing the components, heat treatments, and/or irradiation, pressure). Common polymers are known to have intrinsically poor electrical and thermal conductivity, making them useful as insulating materials. The addition of a conductive filler to the polymer matrix gradually worsens the dielectric properties of the material, which at some point, quite suddenly, becomes conductive; the concentration value at which the insulator-conductor transition occurs is called the percolation threshold. Compounding polymers with conductive fillers has become a method to obtain a wide range of materials with different electrical properties, including those generically called conductive polymer composites. In recent years, there has also been a growing interest in making composite materials using intrinsically conductive polymers, as well as integrating them into a range of electronic devices, including sensors (see [16]).

2.1 Polymeric matrices

All categories of polymers—thermoplastics, elastomers, thermosets, synthetic polymers, or natural polymers are suitable in principle for making polymer matrices, as can be seen from the examples presented below. Elastomeric conductive composites (ECCs) based on carbon fillers are very attractive and play a significant role in the field of smart sensors due to their excellent flexibility, wide sensitivity spectrum, as well as fast response to external stimuli.

A current trend is also the growing interest in biodegradable matrices such as polylactic acid (PLA), giving to the products that incorporate them a lower environmental impact than synthetic polymers.

2.2 Fillers

Combining polymers with electrically and/or thermally conductive nanofillers allows the development of polymer nanocomposites in the form of thin, light, flexible,

wearable films that present interesting electrical and thermal properties for various technical, environmental, and biomedical applications. As conductive fillers for obtaining composite films applicable as sensors in general, various structures are mentioned, as for example Au, Ag nanoparticles, Au or Ag nanowires [2, 8], Ni microparticles [17], and carbon-based materials (e.g., graphene or reduced graphene oxide (rGO) [18], CNT [19] and carbon black (CB)[10], and ceramics (e.g., $Mn_{1.71}Ni_{0.45}Co_{0.15}Cu_{0.45}Zn_{0.24}O_4$ [20]) often together with newer manufacturing technologies such as additive manufacturing (AM) through 3D printing [21].

The appearance of electrical conductivity at the percolation threshold can be explained by a simple intuitive model, in which it is considered that each filler particle is in physical contact with the neighboring ones, thus achieving electrical contact throughout the matrix. Another mechanism for achieving conduction, which explains reaching the percolation threshold at concentrations lower than those corresponding to the physical overlap of the particles, is that of tunneling; in this case, the distance between two filler particles must be max. 1.8 nm [2, 22].

For a given polymer, the electrical resistivity of the resulting composites can be varied over a very wide range by changing the nature and concentration of the filler, as well as the production technology [23]. As the concentration of conductive filler in the polymer matrix increases, the resistivity of the material gradually decreases, reaching a critical concentration (φc) at which the insulator/conductor transition is observed for the studied composite. The value φc represents the conductive percolation threshold, according to the classical theory of percolation. For concentrations of the conductive phase, $\varphi > \varphi c$, the value of φc can be determined with relation (1) [24, 25]:

$$\sigma \propto (\varphi - \varphi_c)t \tag{1}$$

where φ is the electrical conductivity of the composite and t is an exponent that depends mainly on the size of the conductive network in the composite [10].

The decrease in resistivity and the appearance of conductive properties is determined by the formation of conductive networks inside the polymer, in which conductive particles are in electrical contact, allowing the passage of electric current from one conductive particle to another (through tunneling or jumping mechanisms). The maximum distance between particles in such a conductive path has been estimated to be several nanometers [26]. Not all conductive particles dispersed in the polymer participate in the transport of electrical charges through the sample (i.e., they are not effectively involved in conductive paths), but only a considerably smaller fraction than the filler fraction contained in the polymer (**Figure 1**). For example, in the case of CNT, it was estimated that approximately 3.3% of the particles are involved in the effective conduction of the current (being part of the so-called backbone of the electrical conduction (**Figure 2**), in fact, a conductive path similar to those in **Figure 1**, for spherical particles of CB).

The composite materials, also called hybrid materials, are biphasic or multiphase systems, which present special properties, resulting from the synergistic combination of components [1, 27]. Conductive polymer composites have, due to their remarkable properties (e.g., low density, high mechanical strength and corrosion resistance, and controllable electrical conductivity over a wide range, up to values close to the conductivity of metals), numerous applications (e.g., space constructions, automotive industry, sporting goods, electronic devices, electromagnetic shielding, energy storage (safe batteries), overcurrent protections (resettable fuses), filters, and sensors [28])
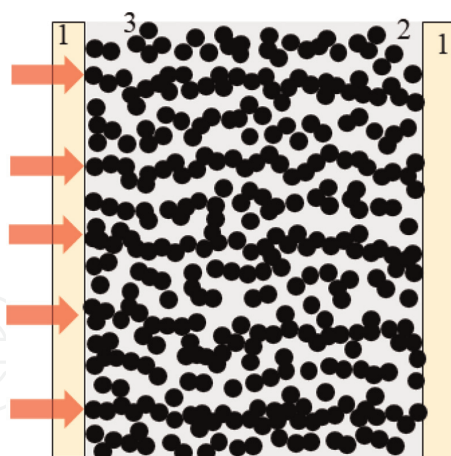
Figure 1.
Possible distribution of small spherical particles (e.g., CB) within a polymer composite: 1—electrodes; 2—polymer matrix: 3—conductive particles (CB). The red arrows indicate the conductive paths which enable the electrons to across the sample. $\vec{E}$ = electric field used to reveal the conductivity.
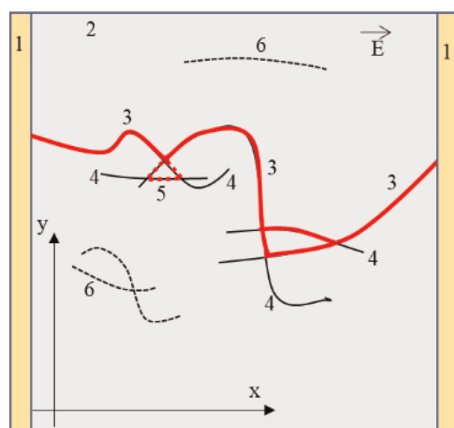

Figure 2.
Possible CNT distribution within a 2D CNT/polymer composite (e.g., a thin film sample): 1—electrodes; 2—polymer matrix; 3—conductive path (backbone of conductive network); 4—zero-current branches; 5—balanced branches; 6—isolated CNT clusters; $\vec{E}$ = electric field used to reveal the conductivity (Adaptation after [26]).

where they have successfully replaced "traditional" materials, such as ceramics or metals [10].

The influence of the filler type, polymer matrices, and dispersion methods on the electrical properties of the resulting CPCs has been reviewed by different authors (see [29] for segregated CPCs, [11] for control methods of electrical properties, and [30] for correlating CPC electrical properties with phase morphologies such as phase segregation or co-continuity [9]).

An effective way to reduce the conductive filler content (or percolation threshold) is to make segregated composites (s-CPCs). The polymer matrix can consist of two thermoplastic, immiscible polymers, e.g., polystyrene (PS) and polypropylene (PP) [31], with the conductive filler (e.g., a carbonaceous material) being preferentially distributed in one of the polymers (PS), and the condition φ_c for the respective polymer is achieved (**Figure 3**). The conductive paths are thus formed at the interface of the two polymers, the composite as a whole becoming conductive at very low concentrations of the conductive filler, compared to homogeneous composites [29]. Other possibilities for obtaining segregated CPCs are shown in **Figure 3**. Comparing
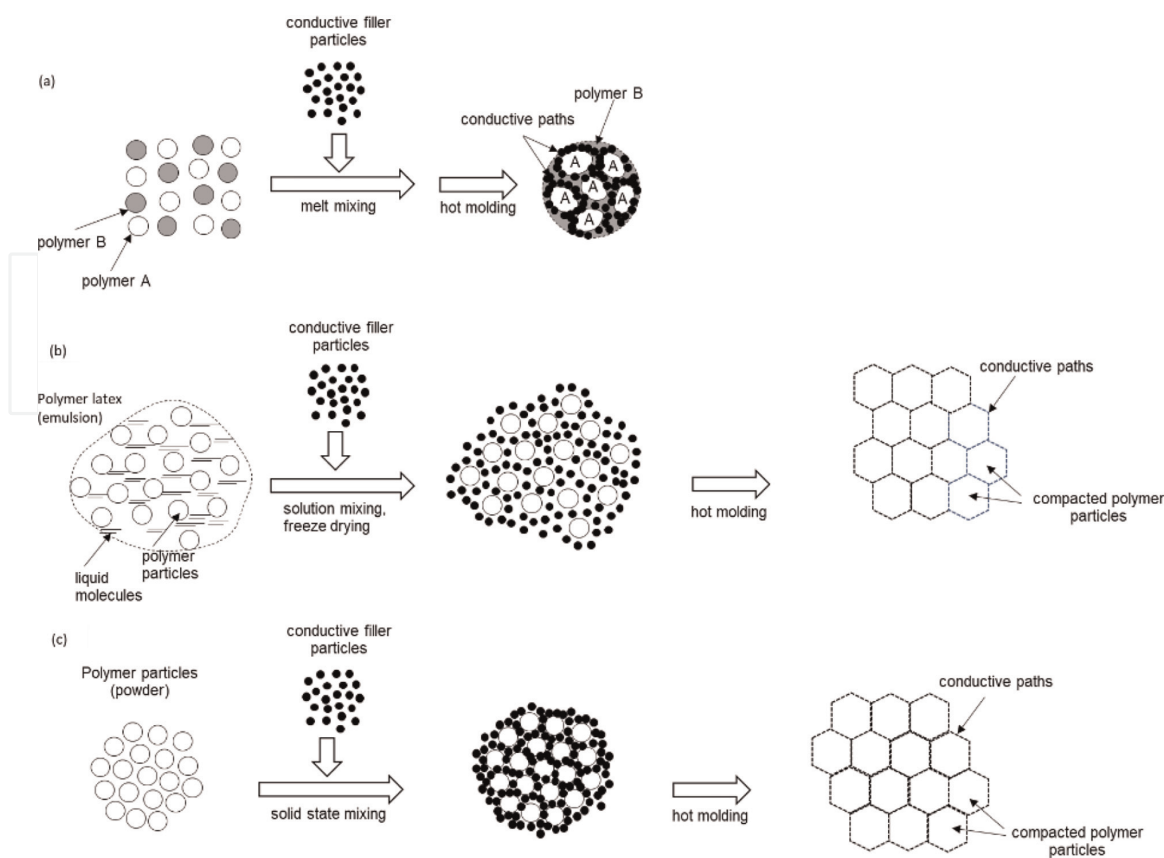
Figure 3.
Three simple ways to produce segregated CPCs: a) melt blending; b) latex technique; and c) dry or solvent mixing (adapted from [29]).

Figures 1 and **3**, it intuitively results that the concentration required to create a network of conductive paths is substantially lower in the case of s-CPC.

Ideally, carbonaceous materials have a structure consisting exclusively of carbon, which can be found in various states of sp^n hybridization, n = 1–3. We must also take into account the fact that, often, there may be heteroatoms (mainly hydrogen or other, oxygen, sulfur, and nitrogen), especially at the edges of extended carbon domains. In general, carbonaceous materials can be characterized by the state of hybridization, as well as by the ratio of the number of hydrogen to carbon atoms (H/C) [32]. Among the carbonaceous materials, those that have potential for use in composites are those that present electrical conductivity. For the sp^3 hybridization state, the typical representative, diamond, does not conduct electricity because all the valence shell electrons move in well-defined directions along the σ bonds. In the case of the other types of hybridization, sp. and sp^2, the electrons in the unhybridized *p*-orbitals have greater freedom of movement and, in the case of extended conjugation effects, can cause the electrical conductivity of the respective substances to appear. It follows that the appearance of electrical conduction will occur in the case of large molecules (polymers or oligomers), in which there may be a large number of conjugated bonds, leading to the formation of molecular orbitals extended on a molecular scale, in which *p* electrons can move practically free.

Sp-hybridized compounds that fall under this condition are polyynes (or carbynes), which formally originate from the polymerization of acetylene and are a linear allotropic form of carbon. However, these compounds currently have a rather theoretical importance, not existing in nature, and their synthesis and stability remain

quite unclear. The only example of synthetic carbyne comes from synthesis in carbon nanotubes, when chains of several thousand sp. carbon atoms were linked to form polydisperse carbyne samples [33–35]. Among the attractive physical properties, the carbine is the unusual electrical transport of electrical charges (negative differential resistance [35, 36]).

Electrical conduction in carbonaceous materials has been studied by different authors and reviewed in a number of papers, such as those by [37, 38]. It is interesting to note that CNTs and graphene nanoribbons show ballistic conduction; that is, the transport of free electrons takes place over relatively long distances (longer than the active length of the medium in which the displacement of charge carriers occurs). Thus, these materials show practically zero resistivity, although they are not super-conductors.

Carbon materials with current practical uses involving electrical conduction have sp^2 hybridization, exhibit continuous conjugation, and can be classified as follows [32]:

- Graphene (Gn) and graphite (Gr), which represent an infinite plane of sp^2-hybridized C atoms and respectively a vertical overlap of such planes that interact with each other through weak van der Waals forces; the p electrons from orbitals not participating in the hybridization are contained in an orbital extended to the scale of the entire graphene plane, their delocalization determining the electrical conduction along the graphene plane as well as the anisotropy of the electrical properties of graphite;

- Graphene fragments (which include nanocarbon and nanographene), which have H/C atomic ratio values between 1 and 0, usually between 0.5 and 1, depending on the degree of development of the carbon skeleton;

- Fullerenes (FLN) and CNT do not contain structural hydrogen, but their hybridization state is slightly different from sp^2, because the morphology of the respective molecules presents curved surfaces; therefore, the hybridization state must be between sp^2 and sp^3 (or to put it another way, the π conjugation is also robust on curved surfaces). Fullerenes are an allotropic form of carbon whose molecules are in the form of closed cages (Cn) formed by rings with 5 or 6 carbon atoms; in each fullerene structure, there are 12 such 5-carbon rings and a variable number, depending on the size of the fullerene, of 6-carbon rings [1].

- Carbon nanotubes structurally belong to the same family as fullerenes. Single-walled (SWCNT) or multi-walled (MWCNT) structures are known, so CNTs can be classified according to the number of graphene layers in their structure. A SWCNT is a cylindrical tube with a diameter of 0.5–1 nm covered by hemispherical ends, which thus appears as a roll, being equivalent to a rolled graphene sheet [39]. MWCNTs comprise several such concentric cylinders, having a diameter of 2–100 nm and a distance between layers of 0.3–0.4 nm. Since the distance between graphite interlayers is similar, MWCNT can be viewed as a folded graphite sheet [40].

- the group of materials generically called amorphous carbon that contains coal in its various forms (coal, brazier, charcoal, etc.), soot, carbon black, etc. These materials are important for industry in general and contain, in addition to C and hydrogen, other heteroatoms such as O, N, or S; taking into account the

composition, carbon fibers can also be included in this group, although structurally, they are more similar to graphite, and the precursor of vapor-grown carbon fiber (VGCF) is very similar to CNT [32].

Graphene, a monolayer (atomic single crystal) structure of covalently bonded sp^2-hybridized carbon atoms, is currently the thinnest material known in the world. Due to its structure, graphene exhibits a series of interesting properties, distinguished by their values, compared to common materials [2, 41], such as: high mobility of charge carriers (electrical conductivity can reach 6000 S/cm, comparable to CNT), high thermal stability ($\sim$2600 K [42]); very good thermal conductivity (5300 W/(m·K) [42]); special mechanical properties: mechanical modulus ($\sim$ 1 TPa) and breaking strength ($\sim$ 125 GPa); gas barrier properties, high transparency, and high-specific surface area [41].

Therefore, graphene has great application prospects and market value in various fields such as electric current transport, high-frequency electronic devices, flexible display, sensors and biosensors, batteries, supercapacitors, aerospace, and biomedical technologies. Graphene is also an ideal nanofiller for reinforcing polymers (composites). Even a small amount of graphene added to the composite causes a spectacular increase in mechanical, electrical, and processing properties [41, 43].

The various known methods for obtaining (synthesizing) graphene are reviewed in the literature (see [43]). Since graphene is difficult to produce (requires a lot of energy and is difficult to structurally control), being consequently expensive, different forms of modified graphene are used in practice (**Figure 4**), such as graphene oxide (GO) and reduced graphene oxide (rGO), as well as graphene wafers, which represent more advantageous alternatives in terms of production costs (see [43, 44] for synthesis of GO and subsequent rGO). Like graphene, these materials can induce great enhancement when combined with polymers, resulting in low-density, corrosion-resistant, low-friction, and low-cost nanocomposites with high-performance and multifunctional properties. However, since the oxygenated groups of GO can significantly affect the properties of the graphene structure, the functionalization of GO is often practiced, whereby the influence of the oxygenated groups is blocked by physical bonds (noncovalent functionalization) or by chemical bonding (covalent functionalization); see more details within the review [43].

Graphene platelets (GnPs) consist of several graphene layers ($\sim$3) overlapped. The assembly has an average thickness of 3.55 $\pm$ 0.32 nm [2, 45], thus being considered a 2D nanomaterial [46]. It exhibits high mechanical strength and high electrical conductivity ($\sim$1400 S/cm), as well as good compatibility with most polymers, as well as preparation of cost efficiency [46]. An interpretation of Raman spectroscopy data in
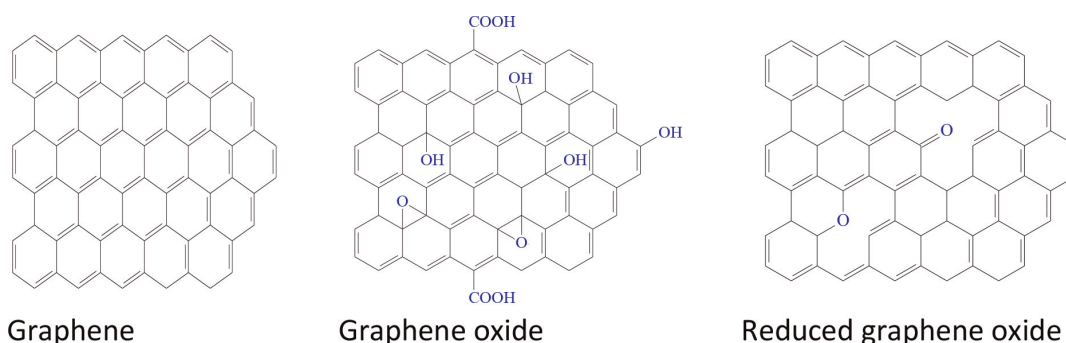

| Graphene | Graphene oxide | Reduced graphene oxide |

Figure 4.
Graphene, graphene oxide, and reduced graphene oxide.

terms of confirming the structure and assessing its integrity [2], compared to GO and rGO, the use of graphene platelets is more efficient in terms of the costs associated with the preparation, as well as the lower concentration of defects compared to GO [45].

A simple method to prepare graphene platelets consists of a thermal shock applied to a graphitic intercalation compound (GIC), followed by an ultrasound treatment [2]. A more detailed description is given in the reference [45].

Polymer/graphene nanocomposites exhibit suitable properties for applications as sensors, and many other electronic and mechanical devices such as capacitors, electromagnetic shielding systems, transistors, electroluminescent devices, batteries, memory, gate dielectric devices, light-emitting diodes, devices with touch screen, and solar cells [41]. A recent review of applied methods for obtaining polymer composites with graphene and modified graphene is presented in the reference [43].

Since the first investigations on the PTC effect in MWCNT/high density polyethylene (HDPE) composites, it has been observed that the presence of CNTs in the polymer matrix can considerably improve the thermal stability of this type of composites due to the interpenetration of the molecular chains of CNTs and HDPE [47]. Carbon nanotubes (CNTs) are thus ideal for inducing electrical conductivity in insulating polymers [26].

The use of CNTs in HDPE matrix composites led to thermistors with significantly better properties (in terms of holding voltage, current through the sample, and response time to applied voltage) compared to commercial CB-based thermistors, with potential critical applications of high temperatures, intense currents, and high applied voltages [48]. However, a problem that arises in the case of using CNT as a conductive filler is the agglomeration of CNT particles, caused by the attraction through van der Waals forces, which results in a reduced value of the weight of CNT particles that effectively participate in electrical conduction (see §2). An effective way to counteract this effect is to modify the surface of the CNT particles. For example, Zhou & Lubineau [49] modified MWCNTs by coating them with a conductive polymer, poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate). After dispersion in a polycarbonate matrix, the electrical resistivity decreased by 11 orders of magnitude for a concentration of 1% (wt), compared to a decrease of only 8 orders for neat MWCNTs at the same loading.

Carbon black (CB) is the most used carbon material for making commercial CPCs, due to its low price, high availability, easy handling, as well as the good electrical conductivity imparted to the polymeric materials in which it is incorporated. However, a number of disadvantages have been identified that limit the exclusive use of CB in high-precision applications such as thermistors, as follows [48]:

- difficult processability of thermoplastic CPCs at high concentrations of CB (>25% wt), specific for obtaining low resistivities ($\sim$ 10 ohm);

- low thermal stability, determined by the susceptibility of CB particles to oxidation at high temperatures;

- poor thermal reproducibility, determined by the random recovery of conductive paths in thermal cycles.

To overcome some of these drawbacks, different solutions have been proposed to improve the properties of CPC with CB, such as: (i) radio-induced cross-linking, for

the stabilization of conductive paths [24]; (ii) the use of mixtures of fillers with a synergistic effect on electrical conductivity [50], in order to reduce the content of conductive charge; (iii) the use of binary, heterogeneous, or homogeneous polymer matrices, in order to obtain the percolation effect at low concentrations of conductive charge or, respectively, to increase electrical reproducibility and improve machinability and mechanical properties; (iv) the use of fillers of a different nature, such as graphite, graphene, or CNT, whose particles having a high aspect ratio and greater electrical conductivity and thermal stability than carbon black can ensure the easier formation and stabilization of conductive paths [48].

The general interest in using carbonaceous materials as conductive fillers in sensor construction is due to their special properties, such as high specific surface area, chemical and mechanical stability, adaptability and functionality, and in the case of resistive sensors, electrical conductivity close to that of metals, as well as good processability with different polymer matrices [10]. Although metal powders are intrinsically more conductive than some carbonaceous materials, such as carbon black, the latter (as well as carbonaceous materials in general) is much more used to obtain conductive composites due to its high chemical inertness. It is known that metal particles tend to undergo oxidation, covering themselves with insulating films of oxides, which results in a decrease in the electrical conductivity of the composite over time [25]. In addition, polymer composite films and sensors with carbonaceous materials (especially those with CNTs and graphene) have promising light weight, flexibility, elasticity, sensitivity, and durability compared to their counterparts prepared with metal nanoparticles. The structure-property relationships of polymer/graphene and CNT nanocomposites and films have been analyzed in a number of previous works [22, 46, 51].

2.3 The effect of temperature on the resistivity of CPCs

Based on the temperature dependence of resistivity, CPC materials can fall into one of the following three categories [52]: (i) PTC—positive temperature coefficient (resistivity increases with temperature); (ii) NTC—negative temperature coefficient (resistivity decreases with temperature); and (iii) ZTC—zero temperature coefficient (resistivity does not depend on temperature). From the multitude of known CPC materials, this chapter deals only with those applicable as resistive temperature sensors with PTC effect (thermistors); more tangentially, certain aspects of NTC sensors will also be covered. Obviously, ZTC materials are not interesting for resistive sensors because their resistivity is independent of temperature.

It is worth to mention that many of the CPC materials that exhibit PTC effect at temperatures lower than the transition temperature may exhibit NTC effect at temperatures higher than the transition temperature [50]. Although PTC materials are often used as self-temperature-regulating heating elements or protective devices with self-limiting current (resettable fuses), micro-switch sensors [52], in reality, in all these applications the respective materials functioning as temperature sensors/thermistors, causing the temporary interruption of the passage of electric current through a certain circuit, when a certain designed temperature is reached, or maintaining an element at a constant, specific temperature. Similar materials with PTC effect can also work as thermometers/temperature sensors, based on a calibration curve, taking into account that their resistance increases with temperature, unambiguously (**Figure 5**).
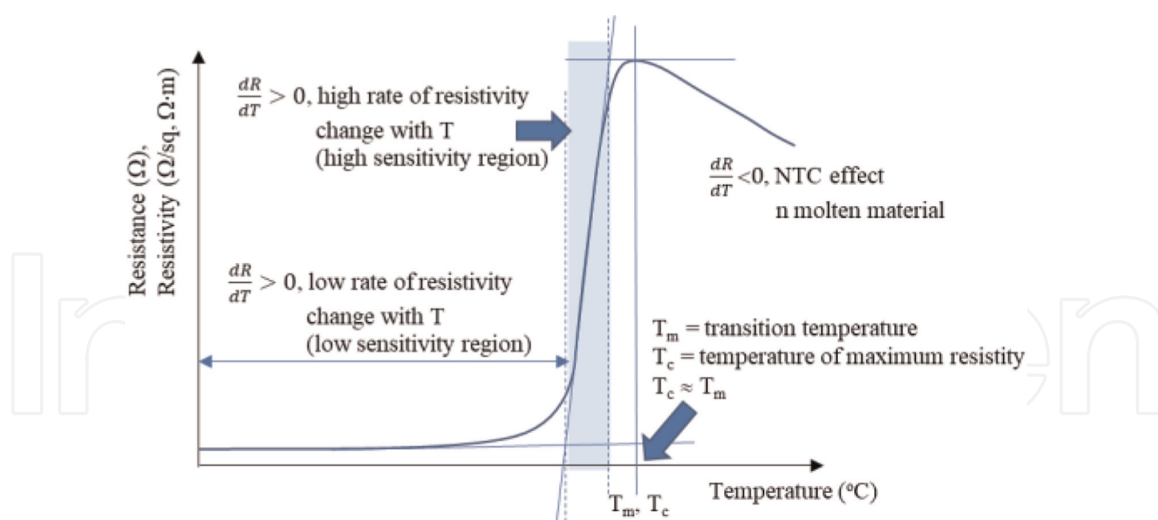
Figure 5.
Resistivity change with temperature for a composite showing PTC effect in solid.

PTC polymer composites have been actively studied due to their high performance and low manufacturing cost. A large amount of research work was initially carried out on PTC materials composed of semicrystalline polyolefins and CB filler, due to the high availability of these materials, easy processability, as well as low resistivity at room temperature [53].

3. Resistive temperature sensors based on CPC materials

Temperature sensors based on the change of some electrical properties can be of different types, such as *pyroelectric* (some ceramic materials or PVdF can generate a temporary voltage when the temperature changes due to the thermoinduced change of an internal polarization state), *RTD* (resistive temperature detector—change in the electrical resistance of a metal with temperature), or *thermistors* (see below) [6]; thermocouples (junction of two dissimilar metals that provide a temperature-dependent electrical voltage), and these are widely used in current practical applications but they appear to be less suitable for miniaturization and nanotechnologies than those already mentioned.

In a classical definition, thermistors were described as devices made of semiconductor materials whose resistance varies with temperature according to an exponential law, within certain limits. Inorganic thermistors were initially made by pressing oxide powders, or their mixtures, followed by sintering at characteristic temperatures. In general, the early thermistors were bulk materials, with NTC effect and allowed the detection of temperature variations of the order of $5 \cdot 10^{-4}$ °C. The characteristic temperature for inorganic thermistors depends on their type and is usually in the range of $-100 \ldots + 300$ °C. More recent literature indicates the use of ceramics (e.g., $Ba_{0.5}Bi_{0.5}Fe_{0.9}Sn_{0.1}O_3$/alumina or $Ni_{0.8}Co_{0.2}Mn_2O_4$/alumina) deposited by screen printing processes resulting in thick film thermistors. This type of thermistors has a considerably smaller size than bulk thermistors, allowing integration in microelectrical circuits [54]. However, the current interest is especially related to organic or hybrid materials, which are more suitable for fine applications in advanced fields such as biomedical and robotics.

Newer materials are conductive polymer matrix composites (CPCs), where the filler can be a metal powder, a semiconducting ceramic, or a carbonaceous material [10, 50]. The operating principle of temperature sensors based on the thermoelectric behavior of CPCs is that, upon heating, the conductive paths of the CPCs change, consequently also changing the electrical resistance (or resistivity/conductivity) of the material [10].

The performance of polymer composites as resistive sensors is closely related to the conduction mechanisms of charge carriers in the conductive filler as such, as well as in the composite as a whole. In general, the key factors that determine the behavior of sensors based on composite materials are polymer properties, conductivity and structural characteristics of the nanofiller, dispersion quality, as well as processing conditions [2].

Since the electrical properties of CPCs depend on the state of the conductive paths in the CPC matrix, the slight change of this state under the action of an external stimulus, such as mechanical deformation, pressure, temperature, and the presence of some liquids (organic solvents), can lead to a significant (measurable and unequivocal) variation of an electrical output signal (resistance, conductivity, and current). Therefore, CPC materials can be designed as sensors for the detection and quantification of external stimuli of the type already mentioned [10].

3.1 Temperature sensors obtained by hot forming (with thermoplastic matrix)

3.1.1 Generalities

Polymer composites for thermistors are conductive materials consisting of a polymer matrix (a single polymer or a mixture of polymers) and a conductive filler (or a mixture of fillers), which give the material electrical conduction properties. Black carbon [10, 25, 50, 55, 56], graphite [50, 57], graphene platelets [28], carbon nanotubes [28], carbon fibers [58], as well as metal powders [59] are commonly used as fillers.

PTC effect thermistors made of polymer composite materials are resistors with positive temperature coefficient of resistivity, applicable as temperature sensors. Depending on how the resistance varies with temperature, two types of PTC thermistors are distinguished: linear and commutative [27]. Linear thermistors are usable as temperature sensors over a wide thermal range, being characterized by a slow, practically linear increase in resistivity with temperature. Switching PTC thermistors are characterized by a steep jump in resistivity at a characteristic temperature and are therefore used as high-sensitivity temperature sensors for narrow thermal ranges located in the vicinity of the characteristic temperature [27]. In applications as resettable fuses or heaters with thermal self-regulation, the respective materials are actually temperature sensors that ensure the functionality of the device as current/voltage protection or as a heating element with self-limiting power [50]. In this regard, the intensity and reproducibility of PTC effects are important factors for the application of temperature sensors [60]. The use of PTC materials as temperature sensors is based both on the slow increase of resistivity with temperature (on the low temperature portion of **Figure 5**) and on the abrupt and strong transition of resistivity at a predetermined temperature (related to a structural transition—melting in case of semicrystalline polymers, glass transition for resins).

In most cases, it is observed that the critical temperature T_c at which the conductor-insulator transition occurs is close to a transition temperature (melting or

glass transition), at which the polymer matrix undergoes a sudden expansion, producing the interruption of the conductive paths [24]. However, for a number of CPC materials, such as those with metal fillers, PTC (resistivity spike) effects have been observed at temperatures significantly different from the transition temperatures of the respective matrices. Such examples can be CPCs with Ag-metallized glass beads filler and polymethyl methacrylate (PMMA) matrix [61], as well as CPCs with Ni-coated graphite filler and polycarbonate (PC) + polycaprolactone (PC) matrix [62], the phenomenon being explained by the large difference between the coefficients of thermal expansion of the conductive filler and the polymer matrix. According to the results of Rybak et al. [63], in the case of nanocomposites with Ag and single matrices of HDPE, or polybutylene terephthalate (PBT), as well as similar nanocomposites with binary matrices HDPE+PBT or HDPE+ Poly(m-xylene adipamide) (MXD6), the T_c value increases substantially with the content of Ag nanoparticles, being between 45 and 180°C. For example, for HDPE-xAg nanocomposites (x = volume percentage), T_c values of 44°C for x = 18% and almost 100 °C for x = 24% Ag. Similar effects were observed for PBT-xAg composites, but at higher temperatures, ranging from about 130 to 175°C, depending on the Ag concentration. Such materials would allow interesting applications as temperature sensors, since the range of maximum sensitivity can be tuned by changing some compositional parameters, such as the nature of the polymer matrix and/or the nature and concentration of the conductive filler.

Despite the fact that composite materials (especially those with thermoplastic or elastomeric matrices) are suitable for industrial applications due to their easy processing, low density, flexibility, and toughness, their use as temperature sensors has been delayed by the poor reproducibility of the resistance values of the materials subjected to repeated heating-cooling cycles in which the temperature of reaching the maximum resistivity (which corresponds to the melting temperature of the polymer matrix of thermoplastic polymers) is exceeded. Thus, the electrical resistance values can differ significantly from one heating cycle to another [50], the phenomenon being explained by the random restoration of the conductive paths during the solidification of the melt. The phenomenon can be effectively countered by radio-induced cross-linking [24, 50], as well as by using polymer mixtures as polymer matrices and/or of mixtures of conductive phases [50]. It should be noted, however, that in the case of heating elements and overcurrent protections, this problem is not so serious, since in practice the material does not reach the melting temperature, the flow of current being practically cut off before the melting temperature is reached [50].

It is also worth to mention that, in the case of thermistors, the obtaining technology is not as simple as in the case of self-regulating heating elements, since even the production of "classical" thin films of uniform thickness (~0.3 mm) is complicated by the high viscosity of composite material melts [24].

3.1.2 Thermistor performance evaluation

Evaluation of the temperature sensing behavior of PTC sensors can be done simply by placing the sensor in a programmable temperature enclosure (which allows heating from ambient temperature to a specific temperature of interest using a heating schedule, usually linear, and which also allows cooling to ambient temperature). The temperature sensor is connected to an electrical resistance measuring instrument, which allows real-time measurements in the range 0 ohm ... T ohm, or more (to be able to detect the maximum resistance at the critical transition temperature). A calibrated contact thermometer (or equivalent) measures the temperature on the sensor surface

(T_t). The dependence curve of the sensor signal (resistance and resistivity) is drawn as a function of the temperature T_t, which, in the case of the existence of a critical temperature in the scanned thermal domain, has the form of **Figure 5**.

To evaluate the performance of resistive temperature sensors, the normalized change in resistance (R_n) can be used, as well as the temperature coefficient of resistance (TCR), defined as follows [3]:

$$R_n(\%) = \frac{R - R_0}{R} \cdot 100 \tag{2}$$

$$TCR = \frac{R - R_0}{R_0} \cdot \frac{1}{\Delta T} \tag{3}$$

where R and R_0 are, respectively, the current resistance and the room temperature resistance and ΔT is the corresponding temperature interval.

It is observed that the signs of the magnitudes R_n and TCR also give the sense of resistance variation with temperature in the considered range: if R_n, TCR < 0, the resistance decreases with increasing temperature, and the material exhibits NTC effect; if R_n, TCR > 0, the material will be PTC.

3.1.3 Examples

Shafiei et al. [28] reported that the preparation of HDPE matrix composites with carbon black filler (18%) and graphene platelets (1%) showed a sudden increase in resistivity between 105 and 120°C, good repeatability, and reproducibility, showing good potential for use as a thermometer, temperature sensor, and heating elements with self-temperature regulation.

Go et al. [60] reported the obtaining of PTC composites with ethylene-vinyl acetate (EVA) matrix and CB filler (0D filler) and exfoliated Gr (2D filler) exhibiting improved intensity and reproducibility at repeated thermal cycling through mobility control filling and thermal expansion due to the combination of fillings. Additionally, these composites exhibited a temperature sensitivity approximately 14 times higher than that reported in the literature for other temperature sensors. The PTC composite with the synergistic combination of 0D and 2D fillers can detect human skin temperature by real-time monitoring and exhibited an accuracy of 0.41°C, thus demonstrating the feasibility of the PTC temperature sensor in specific applications that require sensitivity and relatively high-temperature flexibility, such as monitoring human body temperature.

Polyvinylidene fluoride (PVdF) matrix composites filled with *in situ* thermally reduced graphene oxide (TrGO) and silver nanowires (AgNW) were prepared using solution mixing followed by coagulation and hot thermal pressing [64]. Binary TrGO/PVdF nanocomposites exhibited a low percolation threshold of 0.12 vol % and a low electrical conductivity of about 10^{-7} S/cm. Blending TrGO with silver nanowires led to a significant improvement in electrical conductivity due to the synergistic effect in conductivity of the two conductive materials (the bulk conductivity of TrGO + AgNW materials was higher than the combined conductivity of TrGO/PVdF and AgNW binary composites/PVdF at the same filler content). The hybrid composites showed an increase in resistivity with temperature (PTC), the jump in resistivity being observed at the melting temperature of PVdF. The 0.04 vol % TrGO/1 vol % AgNW/PVdF hybrid material exhibited pronounced PTC behavior, making this composite an interesting candidate for current limiting devices and temperature sensors.

An ingenious sensor is that described by [10], which consists of a poly(chlorinated propylene carbonate)-based polymer foam system filled with CB and cross-linked. This system removes the typical disadvantages related to the nonlinearity and nonmonotonicity of the resistance variation with temperature, specific to PTC composites obtained by randomly dispersing the nanofiller in the polymer matrix. During the heating, the gas bubbles in the closed pores of the foam expand, causing the reduction of the wall thickness and, implicitly, the decrease of the resistivity due to the decrease of the distance between the CB particles. The process of resistance decrease is linear with temperature, reproducible, and reversible (resistivity increases with decreasing temperature).

Lyashkov et al. [65] studied composites with tungsten oxide ceramic ($WO_{3-3.0}MnO_{2-0.5}Na_2O_{5.0}MoO_3$) and polyethylene matrix with ceramic filler volume fraction from 10 to43%. That ceramic was chosen among several WO_3-based materials as having the most nonlinear I-V (*Intensity-Voltage)* characteristic. The obtained composites proved to be isotropic mixtures of filler grains in the polymer matrix and showed high values of the temperature coefficient of strength, in the range of 40–75° C, which depend on both the volume fraction of the filler and the intensity of the electric field. This dependence on the electric field can be explained by the nonlinearity of the I-V characteristic, typical for varistors. In the case of ordinary thermistors, the I-V characteristic is linear, the TCR being independent of the electric field. The dependence of the electrical conductivity of the composite on the volume fraction of the conducting ceramics can be described with a three-dimensional percolation model for a two-phase system.

3.2 Sensors containing a conductive composite with thermoset matrix

Han et al. [2] reported the obtaining of a flexible, high mechanical strength GnPs/epoxy resin composite film exhibiting an electrical conduction percolation threshold of 1.08% (vol) GnPs. Compared to the neat polymer, the composite shows improved mechanical properties (Young's modulus +1344%, tensile strength +66.7%, and good electrical response to bending or twisting up to 180˚). The percolation threshold value calculated for the film of this composite (1.08% by vol.) corresponds to the formation of a global network of connected GnPs inside the epoxy matrix, which ensures the mobility of electrons in the matrix and, implicitly, the insulator/(semi)conductor transformation of the material. After overcoming the percolation threshold, the electrical conductivity of the material increases linearly and steadily with increasing GnPs content due to the creation of numerous conductive paths through the composite. Thus, at a content of 10% (vol.) GnPs, the composite exhibits an electrical conductivity of ∼0.01 S/cm, which corresponds to an increase of 11 orders of magnitude compared to the initial resin. The film acts exclusively as a temperature sensor at T > 20 ˚C, having a linear and stable resistive response in the range of 20–110 ˚C; the temperature coefficient of resistivity is 0.0063 ˚C^{-1}, higher than the standard Pt-based temperature sensor (0.0039 ˚C^{-1}[7]).

3.3 Sensors obtained through additive manufacturing technologies

Additive manufacturing (AM) technologies have completely changed the approach to R&D and production problems in various fields, such as electronics, aerospace technologies, biomedical applications, wearable technologies, and automotive industry. AM enables the faster translation of projects into marketable industrial

products starting from the conceptualization of a three-dimensional (3D) model and reaching the manufacture of printed landmarks. Since AM technologies do not require tools and molds for making landmarks, as is the case for classical technologies, it follows that the application of these technologies can lead to significant savings in materials, time and labor, as well as an increase in the quality and reproducibility of production [16]. Different additive manufacturing techniques such as DIW (direct ink writing), DLP (direct light projection), FFF (fused filament fabrication) or FDM (filament deposition modeling), SLA (stereolithography), and SLS (select laser sintering) are discussed briefly by [16].

A stretchable temperature sensor based on GnPs/PDMS composite, insensitive to mechanical deformation, made by an additive manufacturing technology (3D printing) was reported in the reference [7]. The sensor exhibits a high sensitivity in temperature detection, being characterized by a temperature coefficient of resistance value of 0.0080 °C^{-1}, practically more than twice the TCR value of the standard Pt sensor.

3.4 Sensors based on sandwich structures

Sandwich structures also fall into the category of composites; in this case, the functionality of the material is given by the layers of overlapping materials. Chen et al. [3] recently reported the realization of a flexible sandwich temperature sensor from laser-reduced graphene oxide (LrGO) deposited on a PET support (**Figure 6**). The critical parameters of the sensor fabrication process are the concentration of the aqueous GO solution and the distance between the laser scan lines. For GO reduction, the minimum laser power density must exceed the GO reduction threshold but not reach the level at which ablation of the LrGO layer and PET substrate occurs. A power of 6.5 W and a scanning speed of 2000 m/s were chosen for this purpose for the UV laser with λ = 355 nm. The flexible sensor can be bent on curved surfaces, thus enabling *in situ* temperature measurement, is applicable for monitoring human breathing and space-temporal temperature variation on curved surfaces, and has great potential for realizing noncontact human-machine interfaces.

3.5 Other examples

3.5.1 Wearable sensors

Many of the applications of CNT/polymer composites are as strain sensors [2], but the association between polymer materials and CNTs can produce other interesting
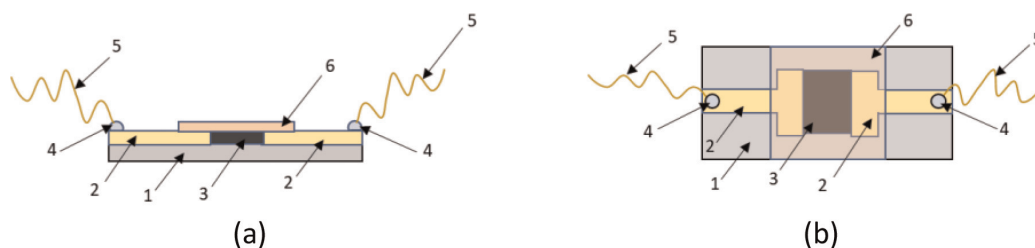

(a)   (b)

Figure 6.
Structure of a sandwiched temperature sensor based on laser-reduced graphene oxide (adaptation after R. Chen et al. 2022): 1—Support polymer film (PET, 0.125 nm thickness); 2—T-shaped gold electrodes (Au/Ti 30/ 20 nm, deposited by sputtering); 3—Laser-reduced (in situ) graphene oxide layer (deposited from aqueous solution); 4—Conductive silver paint (for wire/electrode soldering); 5—Wire; 6 – PI tape (for sensor packaging): a—Side view; b—Top view.

effects for emerging applications. Textiles, as assemblies of fibrous materials, single or multiple, have properties that depend on the nature of the fibers, the treatments applied to them, as well as the method of obtaining—weaving, knitting, or felting (nonwoven textiles). The integration of CNTs in textiles enables the development of wearable technologies and smart textiles, with customizable properties and functionality, through recent approaches to the synthesis of CNT-textile fiber hybrid materials. Such textile materials possess a number of important advantages over ordinary textile materials, such as low weight, integrated nonelectronic regulation of body temperature, self-cleaning without water, and appearance adapted to the requirements of clothing production [66]. Kubley et al. [66] presented a way to synthesize a sheet of carbon nanotube hybrid (CNTH) and tested ways to integrate it into fabrics for various applications, as well as their potential applications in technical and smart textiles.

Continuous monitoring of body temperature is developing rapidly, based on numerous innovations [67]. The use of additive manufacturing techniques enables the large-scale production of flexible temperature sensors, which is now a well-defined direction of development [16, 67]. Another direction is represented by bio-inspired materials and structures, such as octopus legs that have a high ability to attach to skin or other supports [19]. The sensor is resistive type and consists of a hydrogel composite formed by a poly(N-isopropylacrylamide) matrix in which PEDOT:PSS and CNTs are as conducting phases. The NTC sensor has high sensitivity between 25 and 40°C, allowing accurate detection of temperature differences of 0.5 °C and can be used in skin attachment, wearable medical, and health care applications.

3.5.2 Robotic elements with resistive sensors

In robotics, an important concern is the development and production of complex materials that reproduce the functionality of human skin (the so-called humanoid artificial skin), for the development of robots with close human characteristics, as well as for reparative surgery applications. In order to imitate the functionality of human skin, in robotics or prosthetics applications, two complex functions must be ensured, namely (i) detecting the characteristics of the surrounding environment (temperature, hardness, and slip), and the second, (ii) is to grasps various objects to move/condition them. Both of these functions require the existence of a matrix of tactile, force, and temperature sensors connected to a central acquisition system, where the image (map) of temperature and roughness of the environment with which the skin comes into contact will be obtained. Corresponding to the function (i) and based on the environmental information, the force necessary to grasp the target object will be dosed or, if the temperature is outside the established safety range (function II), it will be decided to avoid the contact with it. In addition, the sensor array (just like the skin) must have high elasticity, allowing for bending-rotating movements similar to those performed by the human hand. Obviously, practical realization involves the use of advanced manufacturing technologies such as additive manufacturing and the use of micromechanical systems (MEMS) [40].

Harada et al. [68] made a tactile force sensor (on three axes) in the form of a double 3x3 matrix, which contains a network of temperature sensors and a network of strain sensors. The device obtained exclusively through printing technologies allows the detection of sliding/frictional forces, the sense of touch (pressure), the detection of temperature, as well as the grasping/holding of objects. The temperature sensor (NTC type) consists of a printed CNT/PEDOT:PSS composite, with silver electrodes, and presents a temperature coefficient of $-0.25\%C^{-1}$, in the range of 20–80 °C.

Many of the temperature sensors used to obtain artificial skin exhibit NTC effect [10, 18, 68]. Nuthalapati et al. [69] reported a temperature sensor made of a highly sensitive rGo-Pd/kapton composite, which exhibits NTC effect at Pd contents lower than 1:4 (rGo:Pd) and PTC effect at ratios of 1:6 and 1:8. However, the sensitivity to temperature detection decreases as the Pd content increases.

4. Conclusions

Temperature sensors are key elements in the development of new innovative technologies in actual areas such as wireless health care devices, robotics, smart manufacturing, and smart products. Polymer composite materials with PTC effect are smart materials, with intrinsically abilities of self-limitation of current/voltage and, on this basis, being able to function as smart temperature self-regulating heating elements or as smart fuses. The use of PTC materials as temperature sensors (thermometers) seems complicated by the important nonlinearity of the temperature dependence of the resistivity, but over quite wide ranges, for example, between the ambient temperature and the onset of the resistance steep rise before the critical temperature, the resistance—temperature signal is practically linear enabling the development of interesting applications such as interactive monitoring body temperature with wireless devices.

Conductive carbonaceous materials such as CB, graphite, graphene, CNT, and CF are intensively studied to obtain PTC or NTC resistive temperature sensors in efficient printing-based technologies, to obtain flexible or stretchable sensors, required by new technologies of sensing. The large number of articles published in recent years in relevant publications is a further proof of the topicality of this field.

Acknowledgements

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