Chapter

Preparation and Characterization of Electrically Conductive Polymer Nanocomposites with Different Carbon Nanoparticles

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Abstract

Carbon nanoparticles possess a combination of high electrical and thermal transport properties, as well as low density and different morphologies that make them a good choice to reinforce plastics. Polymer nanocomposites offer great expectations for new and unexpected applications due to the possibility of changing their electrical/thermal behavior by adding nanoparticles while retaining the flexibility and processability of plastics. The possibility of electrical and thermal conduction in a polymer matrix with low amounts of nanoparticles brings opportunity for high demanding applications such as electrical conductors, heat exchangers, sensors, and actuators. Polyolefin nanocomposites offer a significant challenge due to their insulative nature and low affinity for carbon nanoparticles; due to the latter, new production tendencies are proposed and investigated.

Keywords: carbon nanoparticles, polymer nanocomposites, electrically conductive, ultrasound-assisted melt extrusion, thermal properties

1. Introduction

1.1 Carbon nanoparticles

From the discovery of cylindrical nanometric structures composed of one or several layers of carbon atoms similar to graphite by Iijima in 1991 [1], the scientific community embarked on a fascinating multidisciplinary career in the study, synthesis, characterization, and possible applications of these new carbon nanostructures, excited by the unusual combination of properties that these nanomaterials possess, among which the conduction of electricity and heat, low density, high mechanical resistance and morphology stand out. These nanoparticles have diameters in the range of 1 to 100 nm, lengths of 10 to 1000 nm. They can contain one, two or up to 100 layers rolled on each other with an equidistant separation of 0.34 Å [2–4]. Later, Novoselov and Geim [5] made an enormous contribution to science with graphene discovery, whose laminar crystalline structure is composed entirely of carbon atoms with an sp^2

hybridization, with a thickness of only one atom of carbon. Graphene has unusual properties between a metal and a superconductor and high mechanical, elastic, and chemical resistance. Therefore, graphene has been studied and proposed for various applications in electronic, aerospace, automotive, medical, and food industries [6–13].

Due to the ease of modifying its structure by incorporating other chemical elements, hybridization with functional groups, and decoration with organic molecules, carbon nanoparticle applications have been expanded enormously, leading to countless applications. For example, the miniaturization of electrical circuits composed of one or more carbon nanotubes, chemical and electromechanical sensors based on carbon nanotubes, the storage of hydrogen for fuel cells, the increase in charge capacity in batteries based on graphene or graphene nanoplatelets as well as the filtration capacity at the molecular level using graphene-based membranes, besides the reinforcement of polymeric matrices, to name only a few [4, 7, 11, 14, 15].

1.2 Polymeric nanocomposites

Materials science has been searching to generate new materials that possess a balance of properties, making them ideal for new and unexpected applications. Within this vast field are composite materials, which have a continuous phase (metallic, ceramic, or polymeric) and a discontinuous phase (filler or additive), which generally have high filler or additive contents of up to 70%, such as the case of titanium oxide (TiO_2) or carbon black concentrates in a polyethylene matrix, since both additives are used as pigments in the plastics industry [16, 17]. With the beginning of nanotechnology and the growing supply of different carbon nanoparticles, a new class of materials has emerged called polymeric nanocomposites whose advantage lies in using a smaller quantity of particles to modify the behavior of the host matrix or continuous phase.

Electroconductive polymeric nanocomposites were originally based on graphite derivatives, later carbon nanofibers, carbon nanotubes (mono or multilayer), and recently on graphene or graphene nanoplatelets, as well as a wide variety of combinations between these and other nanoparticles with different nature and morphology [8, 17–20]. In order to improve the electrical properties of these materials, combinations of carbon nanotubes have been made with graphite, graphene, clays, copper oxide, titanium oxide, silver nanowires, etc.; in all cases, the aim is to generate three-dimensional networks interconnected to facilitate the passage of electrons or phonons, to generate an electro/thermo-conductive material [21, 22].

In addition to providing the ability to conduct heat and electricity since they can exhibit the Peltier and Seebeck effect, [23, 24] such effects are beneficial in the development of thermoelectric materials, polymeric nanocomposites have also exhibited a noticeable improvement in mechanical properties, a barrier to gases, thermal stability [6, 9, 25, 26] as well as the ability to modify the electrical properties of the host matrix to generate materials for capacitors, electromagnetic and/or radiofrequency shields, have even allowed the development of metamaterials capable of modifying their refractive index, dielectric constant and/or Seebeck effect [27–29].

1.3 Polymeric nanocomposites preparation methods

There are different methods for preparing polymeric nanocomposites, where the main objective up to now has been to achieve adequate dispersion and distribution of carbon nanoparticles that allow modulating the properties of the resulting material. Because carbon nanoparticles are held tightly together by van der Walls forces, different ways have been sought to separate them individually to combine them with a polymer later and obtain a homogeneous polymeric nanocomposite. The main methods employed to achieve this are briefly described below.

1.3.1 Mixed in solution

In this method, the polymer is dissolved in a suitable solvent with the aid of magnetic, mechanical and/or heat stirring to facilitate complete dissolution of the polymer. The carbon nanoparticles are suspended in the same liquid (solvent) or a combination of them, and magnetic, mechanical, or ultrasonic stirring is applied to improve the dispersion of the nanoparticles. Subsequently, both solutions are mixed and kept under stirring, then the solvents are evaporated with heat or slowly in an extraction hood (the above will depend on the nature and reactivity of the solvent). Finally, the resulting material, usually a dark-colored powder, is compacted by applying pressure and heat to obtain a useful material. At the laboratory level, it is the most used method for research purposes; however, the large amount of solvents used makes its scaling at an industrial level unfeasible [30–32].

1.3.2 Polymerization in situ

In this method, one of the monomers or solvents used to obtain the polymer is mixed with the nanoparticles until a homogeneous dispersion is achieved; subsequently, the other reagents, including the corresponding catalysts, are added, and the polymerization reaction is carried out under the conditions of usual temperature and pressure. At the end of the reaction, the product obtained is purified, and the excess solvent is eliminated to recover the polymer formed with the incorporated nanoparticles. Given the complexity of this method, polyethylene's polymerization in the presence of carbon nanotubes at the laboratory level and of polyamide 6 with nanoclays at an industrial level has been successfully reported [20, 33, 34].

1.3.3 Melt mixing

This method is the most widely used at the laboratory level to obtain polymeric nanocomposites; it consists of passing the polymer and nanoparticles through a twin-screw extruder, whereby applying heat, the polymer melts and is transported by the screws that in turn impart shear forces to mix the components, in the different mixing zones that the extruder has. The mixture leaves the extruder, is cooled, and cut to obtain a polymeric nanocomposite. Due to its simplicity, this process can be easily scaled to an industrial level, in addition to the fact that it does not generate waste and does not use solvents [35].

1.3.4 Ultrasound-assisted melt mixing

Given the low affinity of polyolefins and in general of polymers for carbon nanoparticles, modifications have been made to the conventional melt mixing method by applying ultrasound waves in some specific sections of the extruder. It has been reported that this method can significantly improve the dispersion of nanoparticles of different nature and geometry, even with high nanoparticle content [36]. Different variants have evolved; the main difference being the mode of generation and application of ultrasound waves; conventionally fixed frequency ultrasound waves are generated, which are applied constantly or intermittently [37]. In another embodiment, the ultrasound waves are applied constantly, gaining a dynamic frequency sweep in a given interval [35, 38, 39].

There are other methods used for the production of polymeric nanocomposites, mainly at the laboratory level. Nevertheless, the choice of method will broadly define the level of dispersion and distribution of the nanoparticles within the polymeric matrix, and therefore the properties of the resulting material.

2. Methodology

In **Table 1**, the most outstanding reports in electro/thermo-conductive polymer nanocomposites of the last five years are presented to have a broader outlook on the subject. By their nature, polyolefins are good electrical insulators exhibiting

System	σ (S/cm)	Weight (%)	κ (W/mK)	Method of preparation	Ref
PS/SSWCNT[a]	1.25x10^{5}	75	0.30	Ball milling	[40]
PVC/CNT	2.3x10^{-1}	61	0.06	Drop casting	[41]
PP/MWCNT[b,c]	1x10^{-10}	8	—	Melt mixing	[38]
PP/MWCNT[d]	1x10^{-7}				
PP/MWCNT[e]	1x10^{-4}				
PP/MWCNT[f]	1x10^{-3}				
PS-LDPE/MWCNT	2.9x10^{-3}	1.5	—	Melt mixing	[42]
PVC/CNT	2.4x10^{-2}	25	—	Solution	[24]
HDPE/CNT[g]	2x10^{-4}	15	0.60	Melt mixing	[43]
HDPE/CNT[h]	5.8x10^{-5}		0.06		
PP/MWCNT[i,c]	1x10^{-5}	8	—	Melt mixing	[39]
PP/MWCNT[d]	1x10^{-4}				
PP/MWCNT[e]	1x10^{-3}				
PP/MWCNT[f]	1x10^{-2}				
PVC/SG-CNT[j]	3.35x10^{2}	66	0.18	Drop casting	[24]
LDPE/MWCNT	2.38x10^{-2}	5	—	Solution	[44]
LDPE/MWCNT	2x10^{-2}	20	0.67	Melt mixing	[45]
LDPE/GNP	1x10^{-6}		0.58		
PP/CNT[k]	1.6x10^{-2}	2	—	Melt mixing	[46]
PP/CNT[l]	9.56x10^{-1}				
PP/CNT[m]	1.21x10^{-1}				
PP/CNT[n]	1x10^{-3}				
PP/CNT[o]	1.05x10^{-1}				
mLLDPE/MWCNT	2.8x10^{-4}	10	—	Melt mixing	[47]
LDPE/G	1.0x10^{-5}	3	—	Melt mixing	[48]
LDPE/SWCNT	8.3x10^{-5}				
PP/SWCNT	1.21x10^{-1}	2	0.28	Melt mixing	[49]
PP/B-SWCNT[p]	3.58x10^{-1}				
PP/N-MWCNT[n]	4 x10^{-2}	5	0.28	Melt mixing	[28]

[a] *SSWCNT small-bundle-diameter-single-walled CNTs.*
[b] *PP MFI = 34 g/10 min.*
[c] *Melt extruded without ultrasound.*
[d] *Melt extruded with ultrasound fixed frequency.*
[e] *Melt extruded with ultrasound variable frequency.*
[f] *Melt extruded previously dispersed in gas phase.*
[g] *Solid.*
[h] *Foam.*
[i] *PP MFI = 1200 g/10 min.*
[j] *SG-CNT supergrowth-CNT.*
[k] *CNT, NC700.*
[l] *CNT, CNS-PEG.*
[m] *CNT, Tuball.*
[n] *CNT, N-MWCNT A1, Nitrogen doped.*
[o] *CNT, N-MWCNT IFW, Nitrogen doped.*
[p] *Boron doped SWCNT.*

Table 1.
Electric/thermal parameters of the most relevant polymer nanocomposites with carbon nanoparticles.

electrical conductivity in the order of 10^{-12} to 10^{-15} S/cm. As can be seen, different techniques have been used for the preparation of polymeric nanocomposites, achieving fascinating results. It can also be seen that the most popular preparation method is melt mixing, which, as mentioned above, is a versatile and easily scalable method. Another variant that can be observed is that depending on the polymeric matrix; the result will change; even more important is the concentration of nanoparticles used. Another aspect that should be highlighted is the modification or doping of the carbon nanoparticles, which slightly increases this property. Finally, as is known, polyolefins are thermal insulators, and their thermal conductivity ranges between 0.1 to 0.4 W/mK. Thermal conductivity has also shown sharp increases, as shown in Aghelinejad and Leung's reports and Paszkiewicz et al. [45, 50], where the matrix used was polyethylene.

3. Case of study

The motivation of present work was to perform a screening of several carbon nanoparticles to obtain polymeric nanocomposites with a better balance on properties such as electro/thermal conduction, mechanical and thermal stability. For this purpose, different carbon nanoparticles were selected. Their main differences lie in morphology (laminar versus fibrillar), structure (flat versus rolled layers), and functionalization (modified versus un-modified surface, i.e., CNT). Besides, the use of different polyolefins such as polyethylene and polypropylene, which bear significant differences in structure. On the one hand, polyethylene possesses a main chain almost free of pendant groups; meanwhile, polypropylene's main chain contains one methylene group each three carbon atoms. The best candidate is expected to be used to manufacture prototypes of thermistors (temperature sensors based on a change in electrical resistivity).

3.1 Materials and methods

In the following section, the preparation of polymeric nanocomposites in high-density polyethylene (PE) and polypropylene (PP) and their combination with four types of carbon nanoparticles (CNP) are presented and discussed. In all cases, a content of 20% wt/wt of each nanoparticle was used. The characterization results by thermogravimetric analysis, mechanical properties in tension and bending, electrical resistivity, and dielectric constant as a function of frequency and thermal conductivity are also presented. The resins used to obtain the polymeric nanocomposites were the following: high-density polyethylene (PE) Alathon H4620 with MFI of 20 g/10 min and density of 0.940 g/cm^3 provided by LyondellBasell (TX, USA), also polypropylene (PP) Formolene 4111 T with MFI of 35 g/10 min and density of 0.9 g/cm^3 provided by Formosa Plastics, (Tamaulipas, Mexico). The carbon nanoparticles used and their main characteristics are listed in **Table 2**.

The materials' processing was carried out in a Thermo Scientific model PRISM 24MC twin-screw extruder; the diameter of the screws is 24 mm with a length/diameter ratio of 40:1. According to the formulation, a controlled feeder for powders and another for the resin were used, which were previously calibrated to dose the required amount. The addition of the nanoparticles and the resin was carried out simultaneously in the extruder. A screw rotational speed of 100 rpm was used, a flat temperature profile of 180 and 200°C for the nanocomposites with PE and PP, respectively. Under these conditions, a production speed of 3.2–3.5 Kg/h was obtained. To improve the nanoparticle's agglomerates' dispersion and distribution, a device specially designed

Material	Density (g/cm^3)	SSA[*] (m^2/g)	Average length (μ)	Average diameter (nm)	Purity (%)	Supplier
CNT[1]	2.1	200	20	20	90	CheapTubes, Inc
MCNT[2]	2.1	110	20	20	90	CheapTubes, Inc
GNP[3]	2.1	600	2	—	97	CheapTubes, Inc
CB[4]	2.1	240	—	15	95	Cabot Corp.

[*] *SSA, Specific surface area.*
[1] *CNT industrial grade.*
[2] *MCNT, Industrial grade modified CNT with -COOH contain 1.2% of COOH groups.*
[3] *GNP, industrial grade graphene nanoplatelets.*
[4] *Carbon Black, Vulcan XC72 grade.*

Table 2.
Characteristics and properties of the different carbon nanoparticles.

to irradiate the extruded material with ultrasound waves was coupled at the extruder exit. The device consists of a chamber with controlled temperature; inside, there is a 12.5 mm diameter titanium catenoid sonotrode (Branson Corp.) connected to a homemade ultrasound wave generator, which can generate ultrasonic waves in the range of 10 to 50 kHz, with a 750 W power [35, 38]. Finally, the material was passed through a water bath and cutter. Subsequently, each material was compression-molded to obtain a 15 X 15 X 0.2 cm plate, and a PHI press was used, a pressure of 20 Tn, with temperatures of 180 and 200°C for the nanocomposites with PE and PP, respectively. Specimens were cut for the characterization of the polymeric nanocomposites.

The characterization of the polymeric nanocomposites was carried out using the following analytical techniques. The thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer from TA Instruments model Q500, using a sample of approximately 8 mg, a temperature range of 25–600°C, with a heating rate of 10°C/min and an inert atmosphere with nitrogen gas with a flow of 50 ml/min. The mechanical properties were evaluated in a universal testing machine, Instron model 1000, for tension tests in accordance with the ASTM D638 standard, using V-type specimens and a stretched speed of 50 mm/min and a load cell of 10 kN. The flexion tests were carried out according to the ASTM D790 standard using 12 X 1.25 X 0.2 cm specimens in 3-point bending mode; in both cases, five measurements were made, and the average value was reported. The electrical properties of resistance and capacitance were measured with an LCR analyzer in samples of 1 X 1 X 0.2 cm, both faces of the specimen were covered with silver paint, and a copper wire was placed as an electrode. The measurement was carried out at room temperature using a frequency range from 20 Hz to 2 kHz in increments of one decade; 5 measurements were made, and the average value was reported. The thermal diffusivity determination was carried out in a TA Instruments thermal diffusivity analyzer Discovery Xenon Laser Flash model (DXF-200). The analyzed specimen had circular geometry with 12.5 x 2 mm dimensions; both faces were coated with carbon paint and one of them with silver paint to ensure good contact with the temperature sensors; the measurement was carried out in triplicate at 25°C.

3.2 Thermal stability

The study of the thermal stability in electrically conductive materials is of great importance because when an electric current circulates through them, they can undergo heating and alter their behavior or ability to conduct electricity. On the other hand, this analysis makes it possible to determine the thermal stability of the materials and the amount of mass that they can lose due to the effect of temperature in a controlled atmosphere. It should be mentioned that if the atmosphere is air, thermo-oxidative degradation will occur. In **Figure 1**, the corresponding thermograms to the nanocomposites based on PE and PP are presented. While in **Table 3**, the specific data for the mass loss of $T_{5\%}$ and $T_{50\%}$ are shown.

It can be observed that PE exhibits a loss of mass from 330°C, while polymeric nanocomposites exhibit this loss at a temperature around 411°C, regardless of the type of nanoparticle used. It is important to note that the nanocomposite containing CB exhibits the highest thermal stability. For PP, degradation begins at a temperature of 370°C, while for polymeric nanocomposites occurs around 420°C, regardless of the type of nanoparticle used. In this case, nanocomposites based on CNT and MCNT exhibit the highest thermal stability of all.

Various reports in the literature suggest that carbon nanoparticles provide greater thermal stability or heat resistance to polymers in general due to a mechanism based on the formation of a carbonaceous layer and a tortuous path similar to a labyrinth on the surface of the material that prevents the release of combustion gases [19, 26]. This analysis is of great importance for flame retardancy applications in aeronautics, automotive, and textile industries and to determine the safety temperature that the material can support before molten and inflamed by the passage of an electrical current.

3.3 Mechanical properties

The mechanical properties of polymeric nanocomposites are of great interest because, as mentioned above, the addition of carbon nanoparticles can improve

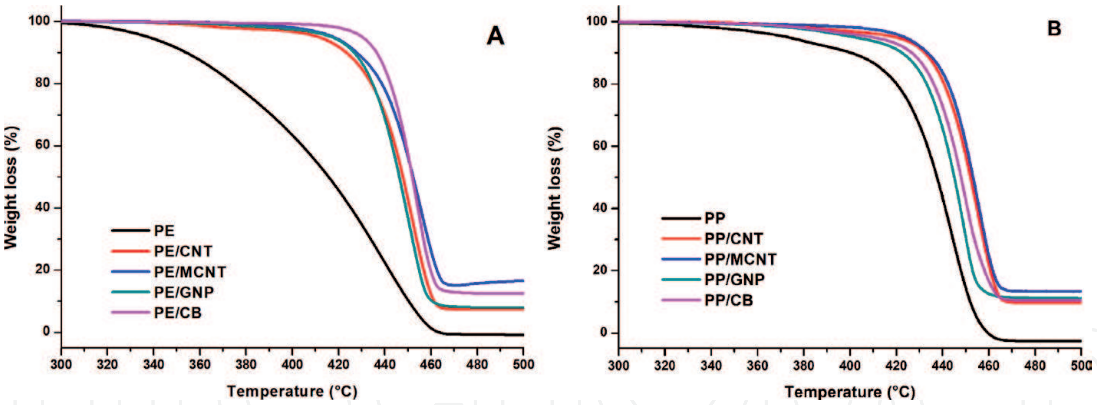

Figure 1.
Thermal stability by TGA of polymeric nanocomposites with 20% wt/wt of different CNP, (A) PE base, and (B) PP base.

Material	Polyethylene		Polypropylene	
	$T_{5\%}$	$T_{50\%}$	$T_{5\%}$	$T_{50\%}$
Polymer	337.50	415.67	373.49	437.59
CNT	411.28	447.81	420.09	451.99
MCNT	417.68	452.17	423.69	453.15
GNP	416.88	446.27	402.26	445.07
CB	430.27	451.89	419.47	449.98

Table 3.
Degradation temperatures at $T_{5\%}$, $T_{50\%}$, of polymeric nanocomposites with different carbon nanoparticles.

Material	Polyethylene			Polypropylene		
	Tensile modulus (MPa)	Elongation (%)	Flexural modulus (MPa)	Tensile modulus (MPa)	Elongation (%)	Flexural modulus (MPa)
Polymer	23.68	747	376	33.28	571	289
CNT	41.99	1	965	43.05	1	862
MCNT	38.84	1	989	38.7	1	800
GNP	42.03	1	1052	42.13	1	980
CB	40.47	1	951	44.22	1	913

Table 4.
Mechanical properties of polymeric nanocomposites with different carbon nanoparticles.

their performance. In **Table 4**, the properties of the PE and PP-based nanocomposites with the different carbon nanoparticles are listed.

As expected, with the addition of nanoparticles, the different properties were modified; firstly, the PE exhibits a tensile modulus of 23.68 MPa, while the nanocomposites present a maximum increase of 180%, this increase in resistance to stress causes the elongation of the material to be markedly reduced, suggesting that the stiffness of the material has changed from a ductile to a brittle material, in which plastic deformation has been suppressed. For its part, the flexural modulus corroborates the above since PE has a value of 376 MPa, and in nanocomposites, this value has increased to 280%. A similar behavior occurs with PP, exhibiting an increase of 130% and 330% in the tensile and flexural modulus, respectively. In this sense, the greatest increase in mechanical properties for polyethylene is obtained with GNP > CNT > CB > MCNT, while for polypropylene, it is CB > CNT > GNP > MCNT. In this sense, it is worth mentioning that the surface modification made to the MCNTs did not improve by itself, the compatibility with the host matrix PE or PP.

In the literature, many reports can be found that mention the improvement in mechanical properties in polymeric nanocomposites reinforced with carbon nanoparticles. However, the addition of compatibilizing agents such as maleic anhydride grafted to the resin is required to achieve a substantial increase in the mechanical properties, even with low amounts of carbon nanoparticles [9, 26, 51, 52]. Due to the lightweight and high modulus obtained by the polymeric nanocomposites reinforced with carbon nanoparticles, aeronautics and automotive industries would be benefited from the development of these materials for different components, which can provide a reduction in weight and lower consumption of fuels.

3.4 Electrical properties

The evaluation of electrical properties was carried out using an LCR as a function of a frequency interval, as shown in **Figure 2**. First, the polyethylene-based system allows observing that the PE resin exhibits the highest electrical resistance values at low-frequency values; above 10 kHz, the material becomes polarized and shows a lower electrical resistance, which decreases three orders of magnitude when reaching 2 MHz. With the addition of GNP, the material exhibits a behavior similar to that of PE, one order of magnitude lower in terms of electrical resistance. Meanwhile, the materials that contain MCNT and CNT show a reduction of 7 and 8 orders of magnitude; however, the polarization effect occurs when reaching high frequencies of 100 kHz. The CB-based system exhibits the least electrical resistance with nine orders of magnitude reduction concerning PE alone. In addition to not

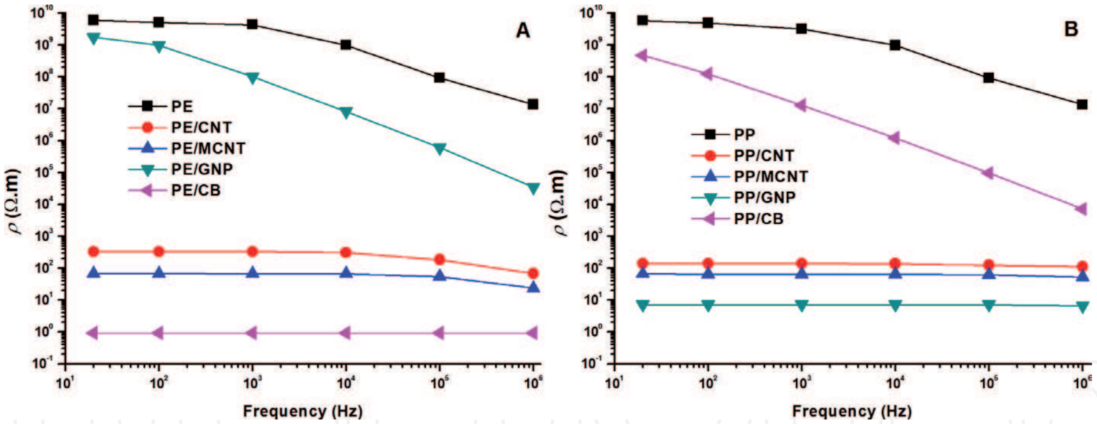

Figure 2.
Electrical resistance as a function of frequency, of polymeric nanocomposites with 20% wt/wt of different CNP, (A) PE base, and (B) PP base.

showing polarization effects as a function of frequency, which suggests that it behaves as an excellent electrical conductor.

For materials based on PP, the behavior is slightly different PP only presents the highest values of electrical resistance at low-frequency values; above 10 kHz, the material is polarized and shows a lower electrical resistance, which decreases three orders of magnitude when reaching 2 MHz, in the same way as the PE. Surprisingly, the CB-based system exhibits an electrical resistance that is completely dependent on the frequency. When it increases, the electrical resistance decreases to four orders of magnitude concerning the PP, suggesting that the material behaves like a semiconductor. On the other hand, the materials that contain CNT and MCNT show a reduction of seven and eight orders of magnitude without presenting the polarization effect in the entire frequency range, which suggests that they behave like a good electrical conductor. Finally, the compound containing GNP shows the lowest electrical resistance with a reduction of nine orders of magnitude and a linear response throughout the entire frequency range used. Based on the above, it can be pointed out that the nature of the polymeric matrix and the type of carbon nanoparticle can notably modify the electrical behavior of the polymeric nanocomposite [8, 31, 53, 54].

The behavior of the dielectric constant of polymeric nanocomposites is presented in **Figure 3**. Analogously to the behavior of electrical resistance, the dielectric constant follows a similar trend with the addition of carbon nanoparticles. The PE has a value of 3 and a linear behavior in the entire frequency range, while the nanocomposite with GNP shows an increase of 1 order of magnitude and a linear behavior as a function of frequency. Materials containing CNT and MCNT show an increase of three orders of magnitude for PE, with a slight decrease at high frequencies. The material that contains CB exhibits a frequency-dependent behavior since, at 20 Hz, it shows an increase of four orders of magnitude and then it decreases two orders of magnitude from a frequency of 1 kHz; this behavior corresponds to that of a capacitor, capable of storing energy and releasing it suddenly when used in electrical/electronic circuits.

On the other hand, PP exhibits a dielectric constant of 3 and does not vary as a function of frequency; the nanocomposite with CB shows an increase of one order of magnitude with respect to pure PP, while the nanocomposites with CNT and MCNT show an increase in 3 orders of magnitude and a slight decrease at high-frequency values. Finally, the nanocomposite with GNP presents the highest value of dielectric constant, with an increase of up to four orders of magnitude at a frequency of 20 Hz, and decreases by one order of magnitude for the rest of the frequencies evaluated. Similar to the behavior of PE nanocomposites,

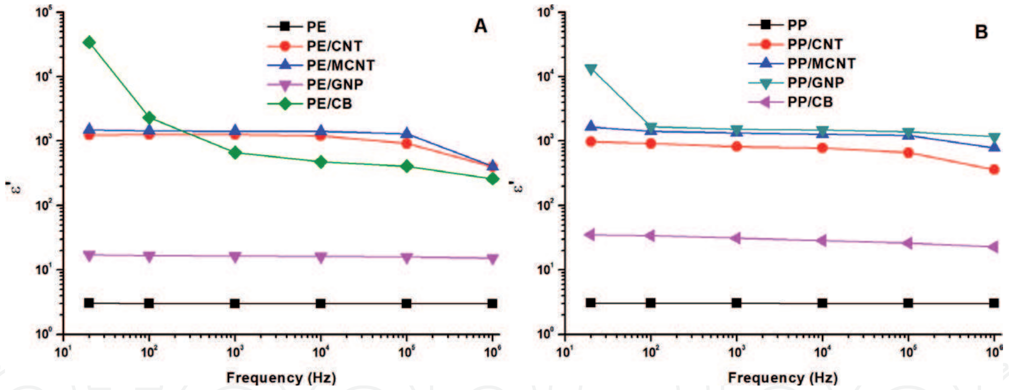

Figure 3.
Dielectric constant of polymeric nanocomposites with 20% wt/wt of different CNP, (A) PE base, and (B) PP base.

PP-based nanocomposites exhibit capacitor-like behavior throughout the evaluated frequency range.

The combination of properties for these new nanocomposite materials results in various applications that had not been previously conceived. For example, supercapacitors can be manufactured for systems that require a precise regulation of the supplied energy and a high energy storage capacity, and that in this way, the energy necessary to drive an electrical component can be supplied without the need to overload the electrical network of the circuit, besides not present a memory effect [25, 31]. Another field of interest for those materials would be the packaging industry, with the development of antistatic, static dissipative or semiconductive packages, for the protection of electronic components during their transportation, even for EMI or RF shielding for aerospace and defense to protect safety- and mission-critical systems from intentional and unintended electronics emissions [44]. The growing industry of electronic textile or smart textiles that develop wearable technology requires integrating textile fibers capable of conducting electrical signals. There are fabrics in which electrical and electronic elements such as microcontrollers, sensors, and actuators have been integrated that allow clothing to react, send information, or interact with the environment [55–57].

3.5 Thermal conductivity

The study of the thermal properties of polymeric nanocomposites intended for electronics applications is of great importance since, as mentioned above, the passage of electric current can induce a temperature gradient in electrical conductors, even in metals. The heat capacity was first determined, as well as the density and thermal diffusivity to determine the thermal conductivity of polymer nanocomposites. Values are shown in **Table 5**.

According to the data reported in **Table 5**, PE has the highest value of Cp; with the addition of the different nanoparticles, the Cp of the nanocomposites decreases significantly, the most notable case being the nanocomposite with CB. Meanwhile, PP exhibits an even higher Cp than PE, while the addition of the different nanoparticles promotes a decrease in this value, with graphene nanoplatelets being the material that most reduces this value. The decrease in Cp of the different nanocomposites can be associated with the ease they present for heat conduction, making the material less thermally insulating.

On the other hand, the thermal conductivity presents substantial improvements; in general, the PE-based nanocomposites exhibit the most significant increase in

	Polyethylene		**Polypropylene**	
	Cp (J/gK)	**κ (W/mK)**	**Cp (J/gK)**	**κ (W/mK)**
Polymer	1.846	0.24	1.917	0.28
CNT	1.671	0.43	1.672	0.32
MCNT	1.643	0.25	1.639	0.34
GNP	1.736	0.31	1.477	0.25
CB	1.495	0.28	1.569	0.30

Table 5.
Heat capacity (Cp, J/g K) and thermal conductivity (κ, W/m K) of polymeric nanocomposites with different carbon nanoparticles.

thermal conductivity 79, 29, 16, and 4% for the nanoparticles in the following order CNT > GNP > CB > MCNT, suggesting that carbon nanotubes are the most effective additive to increase the thermal conductivity of the nanocomposite. The trend is reversed, with increases of 21, 14, 7, and − 11% for MCNT > CNT > CB > GNP for PP-based nanocomposites. Although the Cp of the nanocomposites follows a different trend towards thermal conductivity, it should be mentioned that the type of polymeric matrix, the morphology, distribution, and dispersion of the different nanoparticles play an important role in heat conduction. This phenomenon is carried out through phonons; therefore, if there are spaces in the material in which the nanoparticles are too far apart, the phonons' passage through the material will find a physical barrier for their passage.

Recent reports suggest that a polymeric nanocomposite's thermal conductivity can be affected by different factors, including the processing method, the number of defects in the carbon nanoparticles, and, finally, their dispersion within the polymeric matrix [21, 29, 45, 46, 58]. The capability to conduct heat in a polymeric nanocomposite makes an ideal candidate for different applications such as heat exchangers, solar water heaters, thermoelectric materials, electrical heaters, to mention a few [22]. These devices will take advance of the lightweight, mechanical strength, thermal and dimensional stability of these materials, in which automotive, construction, and green industries are interested.

3.6 Thermistors

The electrical resistivity of polymeric nanocomposites with carbon nanoparticles shows an anomalous increase near the melting point of the matrix; this effect is known as a positive temperature coefficient (PTC) of resistivity. On the other hand, the negative temperature coefficient (NTC) is a very sharp decrease in resistivity when the temperature is above the melting point of semicrystalline polymers. These kinds of materials have important industrial applications like overcurrent protectors and self-regulating heaters [59, 60].

The polymer nanocomposites obtained were evaluated for their potential use as a thermistor. For this purpose, a prototype will be constructed; it consists of a square piece with dimensions 1 X 1 X 0.2 cm; both sides were cover with silver paste as an electrode and a copper wire. Kapton ® tape was used to cover the prototype and isolate the wires during the heating cycle. A Mettler Toledo FP82 Hot Stage was used to supply heat in an interval from 40 to 160°C at a heating rate of 5°C/min, the Hot Stage was connected to a Mettler Toledo FP90 Central Processor, the electrical resistivity was measured with a Keithley Source Meter model 2400, in a 4-wire sense mode, to avoid the parasite signal in the circuit.

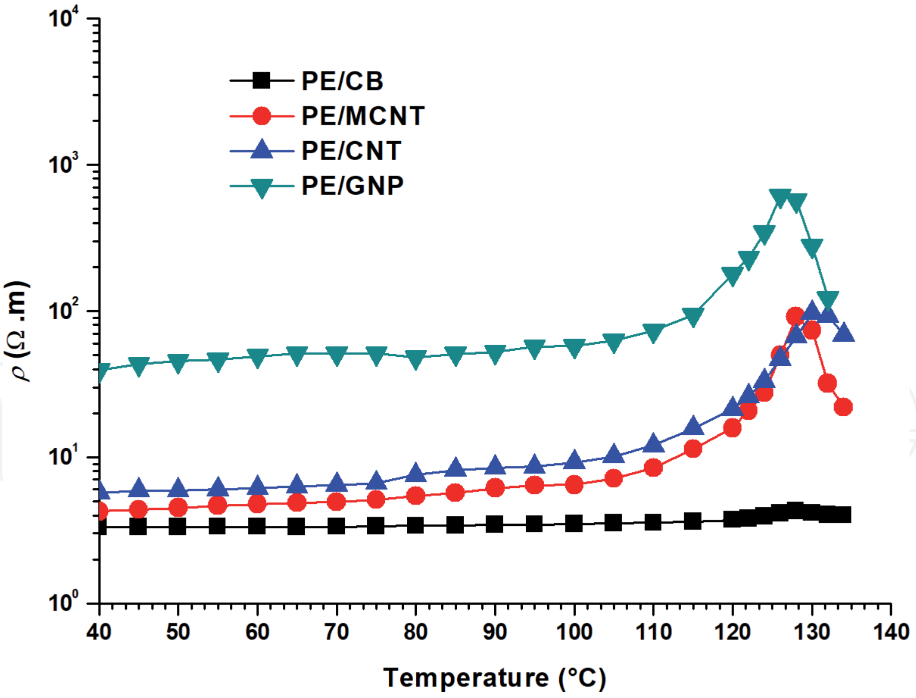

Figure 4.
Temperature versus electrical resistivity of PE base polymeric nanocomposites with 20% wt/wt of different CNP.

As seen in **Figure 4**, all the polymer nanocomposites exhibit thermistor behavior, i.e., an increase of resistivity around 128°C. The intensity of the PTC (the electrical resistivity ratio at the melting point versus room temperature) depends on the type of carbon nanoparticle used. The interval of temperature at which this phenomenon occurs is between 127 and 131°C. In this sense, the intensity of the PTC is in the following order GNP > CNT > MCNT > CB. This behavior could be associated with the capability of the polymer chains to break apart the conductive pathway formed in the polymer nanocomposite, due to the semicrystalline nature of the polymer matrix and the reduction in viscosity, during the heating. It is worth mentioning that PE/CB nanocomposite exhibits the lowest PTC intensity, probably due to the high structure of the CB (CB possess the small average particle size) and could form new conductive pathways in the molten state as stated by Zeng et al. [61].

4. Conclusions

The polymer nanocomposites with carbon nanoparticles become an electrically conductive material whit the addition of a certain amount of carbon nanoparticles; this property is fundamental in electrical and electronic applications. For many years, carbon black has been chosen as the best candidate for this purpose; with other carbon nanoparticles such as CNF, CNT, GO, graphene, and their combination with other materials, significant improvements have been made for electrically conductive materials.

In this work, the preparation and characterization of electrically conductive polymeric nanocomposites with different carbon nanoparticles was addressed to screen the type of carbon nanoparticles that allows them to obtain polymeric nanocomposites with a better balance on properties such as electro/thermal conduction, mechanical, and thermal stability. A material with the desired properties for their application in electronics, such as low electrical resistivity, thermal stability, and mechanical strength, besides thermal conductivity, is PE/CB polymeric nanocomposite since it exhibits a better balance of properties. This set of properties makes them candidates for use in various applications. Besides thermistors, they may be candidates for use in electrical heaters, which are a kind of electrical resistor used to converts electrical energy into thermal energy, as thermoelectric materials for their use in the exploitation of renewable energies, in heat exchangers, as EMI and RFI shielding, and as a wearable textile for smart applications.

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Conflict of interest

The authors declare no 'conflict of interest'.

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