

## Research Article

# Relationship between Polymer Dielectric Constant and Percolation Threshold in Conductive Poly(styrene)-Type Polymer and Carbon Black Composites

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Received 4 June 2015; Revised 4 August 2015; Accepted 5 August 2015

Academic Editor: Wei Liu

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We study the effect of dielectric constant of some poly(styrene)-type polymer matrix on the percolation threshold in conductive polymer composites with carbon black (CB). We demonstrate that percolation threshold diminishes with an increment of the dielectric constant of polymer matrix. We chose polystyrene and other three polymers similar in structure and molecular weight but with different chemical nature. The corresponding dielectric constant and critical concentration,  $X_c$ , in volume fraction of carbon black, v/v CB, were the following: 4MePS ( $\epsilon = 2.43$ ;  $X_c = 0.058$ ), PS ( $\epsilon = 2.60$ ;  $X_c = 0.054$ ), 4BrPS ( $\epsilon = 2.82$ ;  $X_c = 0.051$ ), and 4ClPS ( $\epsilon = 2.77$ ;  $X_c = 0.047$ ). The correlation between both parameters confirms that the percolation threshold decreases while the dielectric constant increases. At microscopic level, this effect is attributed to an enhanced physical interaction of the CB particles with the asymmetric electric density produced by electronegative or inductive atoms/groups. Therefore, by controlling the chemical structure of the polymer matrix, the attraction forces between the polar groups on the carbon black surface particles with those of the polymer matrix can be improved, which in turn induces a better disaggregation and dispersion of those particles into the polymer matrix, allowing the percolation threshold reached at a lower filling fraction.

## 1. Introduction

Polymer composites with electrical properties have received attention during the last 60 years for scientific and technological reasons [1–7]. From the theoretical point of view, the electrical conductivity of these materials can be explained very well by the percolation approach. This predicts the formation of electrical pathways at the critical filling fraction  $X_c$ , and for larger filler fractions the electrical properties fit very well with the following equation [8]:

$$\rho(X) \approx (X - X_c)^{-\beta}. \quad (1)$$

With  $X$  being the volume fraction of the conductive particles,  $\beta$  is the critical exponent and  $X_c$  is percolation concentration or critical concentration. Characteristics of the shape and

spatial distribution of the conductive particles used for the composite system can be related to the value of the critical parameters [8–12].

For these materials, both the fillers and the polymer are very important for designing and good performance. Some factors concerning the conductive particle nature must be considered in conjunction with the polymer properties such as thermodynamic and rheological ones and with the processing conditions employed for the composite preparation. The filler content must be as low as possible to avoid problems such as poor processability, poor mechanical properties, high cost, and particle-polymer incompatibility, which lead to weakening of some properties including the electrical ones. In order to decrease the three-dimensional percolation threshold and optimize the polymer-particles compatibility,

several studies have been realized considering the conductive particles and/or the polymer matrix. Studies related to conductive particles are *nature* (metallic, carbonaceous, polymeric, etc.), *geometry* and *size*, *surface functionalization*, and so forth [5]. The main problem during the construction of the conductive network when carbonaceous particles are used, such as carbon black [6], graphite [7, 13, 14], fibers [15, 16], or carbon nanotubes (NTC) [17, 18], is the van der Waals interactions among carbon particles in the macroscopic agglomerates, which has a crucial effect for obtaining an optimal dispersion of them into the polymer matrix and in turn in the percolation threshold. Then, the compatibility is related to composition and surface chemistry [19]; *geometry*: a high aspect ratio of the conductive particles allows reaching lower percolation concentrations [14, 20]; *structure* [10, 21–23]: a higher structure of the primary aggregates of elementary carbon particles reduces percolation threshold due to a better electric path interconnection at microscopic level [10]; *surface area* [22, 23]: surface functionalization of the NTC [24–28], graphite [14, 29], and CB particles [22] has been used to enhance the dispersion and compatibility with polymer matrixes. However, chemical modification is used to reduce electrical properties of conducting particles.

Some other studies have taken into account the polymer matrix characteristics as *viscosity*, *molecular weight*, and *superficial tension*. Matrix melt viscosity has two effects: it can either reduce or increase percolation threshold, depending on particle size and shape. In carbon black filled polymers, percolation threshold increases with melt viscosity [30–34]. (2) The *crystalline degree* [18, 35, 36] of the polymer matrix becomes important for the percolation threshold in carbon black polymer composites, and segregation occurs preferably on the amorphous phase. For this reason, percolation threshold could be reached at lower volume fraction of carbon particles in semicrystalline than in amorphous polymers; (3) *cross-linking*; (4) *elastic modulus* [37], and (5) *immiscible blends* in which composites show enhanced interparticle connectivity around the incompatible region and consequent decreasing of the percolation threshold due to a preferential distribution of the conductive carbon along the interface of those immiscible polymers [20, 38–42].

The preparation method also has an influence in the dispersion process of the conductive particles and as a consequence in the reproducibility of the electric properties of the respective polymer composites. Most of the polymer composites are produced in liquid phase, in a melt stage, or in monomer or polymer dissolution. In both cases, a suspension is always formed and it has been studied that the resistivity control for melt polymer composites is also dependent on processing parameters such as mixing time, temperature, rotor speed, molding time, temperature, and pressure at molding [43–49]. For a composite obtained by *in situ* method that consists in making first a dispersion of carbon particles into the monomer and then a subsequent polymerization of that suspension, the optimization of the processing parameters is more difficult. In solution, particles are immersed in a viscous fluid and they are submitted to interactions which may strongly change their distribution [50] depending on the stirring speed, solvent proportion, temperature, ultrasonic

time, ultrasonic oscillation frequency, and external variables like electric fields [51, 52].

For electrical properties of polymer composites, a variable of interest that has not been deeply studied is the role of the structure (chemical nature) of the polymer matrix that surely plays in junction with the aforementioned parameters during the dispersion/distribution process of carbon particles. Due to the existence of secondary interactions between the superficial functional groups on carbon black and the chemical groups on the polymer, that interaction could be improved or maximized with the presence of certain function on the polymer. At the end, any functional group(s) could modify the electronic density of the molecules in some magnitude which could have a positive or negative effect on the formation of conductive paths for the formation of polymeric compound as will be shown below. There are few studies that show a qualitative effect of the chemical influence of the polymer matrix on the percolation threshold [39, 53–56] but without any clear tendency. Because we are interested in evaluating it in terms of a macroscopic property of the polymers, the dielectric constant and the results are interpreted in terms of the existing theories. The magnitude of the dielectric constant is dependent on the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. At optical frequencies ( $10^{14}$  Hz), only the lowest mass species, electrons, are efficiently polarized. At lower frequencies, atomic polarization of heavier, more slowly moving nuclei also contributes to the dielectric constant. Atomic polarization of induced dipoles can occur in the infrared ( $10^{12}$  Hz) or lower frequency regimes. Dipole polarization is the reorientation and alignment of permanent dipoles in response to the electric field. The three modes of polarization can interact, but, in most cases, they act essentially separately and are therefore additives. The dielectric constant measured at frequencies lower than optical frequency can lead to a basic understanding of the influence of molecular structure on dielectric properties in polymers [57–60]. It is because we propose to study this polymer property in the control of the electric percolation threshold on polymer composites using one type of CB particles, Vulcan XC72, which has polar nature and is widely used by other authors for its high structure and some surface oxidation. The proposal consists in obtaining polymer composites from polymer matrix of different dielectric constant produced by the presence of electronegative or inductive atoms/groups into the aromatic ring which is the base of the polystyrene polymer. These polymers were synthesized by the same method in order to have very close molecular masses. The preparation method for CB polymer composites was in solution by ultrasonic shaking (solution) [56]. Carbon black particles were dispersed in polymer solutions at the same viscosity and they were shaken in the same time depending on the CB amount in order to control the processing parameters and to obtain them in reproducible way. From the microscopic point of view, CB particles should be attracted and better distributed by more polarizable (higher dielectric constant) polymers producing conductive networks at lower CB concentration than those

composites based on polymers with a reduced dielectric constant. We demonstrate a close correlation between the CB percolation threshold and the dielectric constant of some poly(styrene)-derivatives polymer matrixes, which make the electronic affinity between polymeric matrix and CB particles clear, evidencing a better dispersion and a preferential distribution of the carbon particles in highly polarizable polymer matrixes. This effect has a positive consequence in the electrical properties by lowering the concentration threshold. In order to avoid, as much as possible, the influence of other factors on the percolation threshold, such as molecular weight and density among others, polymer matrixes were synthesized via free radicals in bulk medium for producing amorphous polymers under the same reaction conditions. Structural and electric characterizations were also complemented by thermal analysis as differential scanning calorimetry, DSC, and thermogravimetric analysis, TGA, and density and molecular mass. Dielectric constant was evaluated as a function of temperature at a low frequency (850 MHz) in order to analyze the dipole effect of the repetitive polymer units.

## 2. Materials and Methods

**2.1. Materials.** Styrene, 4-methylstyrene, 4-chlorostyrene, and 4-bromostyrene monomers were purchased from Aldrich. Inhibitor was eliminated by surpassing the liquid monomers through a chromatographic type WB2-basic Alumina packed column. Tetrahydrofuran (THF) and benzoyl peroxide (BPO) were also supplied by Aldrich. CB Vulcan XC72, with a size of 32 nm and a density of  $1.8 \text{ g/cm}^3$ , was donated by Cabot Co. and it was used as received.

**2.2. Synthesis of Matrix Polymers.** Polymerization of monomers after being free of inhibitor was carried out in mass via free radicals using benzoyl peroxide (400:1 mol monomer : BPO) as initiator, and the following temperatures were used in an oil bath under a nitrogen flux: first, monomer was left at  $70^\circ\text{C}$  for 12 h; then, the high viscose product was left for 8 h at a temperature of  $90^\circ\text{C}$  and finally temperature was elevated at  $110^\circ\text{C}$  and the solid product was left for 8 h. After cooling to room temperature, the solid polymer was solved in THF and reprecipitated from methanol in order to remove residual monomer and initiator. The white solid was filtered, washed with methanol, and dried under vacuum for 72 h. Polymers (Figure 1) obtained were characterized by DSC, TGA, Gel Permeation Chromatography, GPC, and density, and dielectric constant was measured at 850 MHz.

**2.3. Composite Preparation.** All composite samples were prepared by the same procedure to avoid fluctuations in the evaluation of critical CB concentration. Composites from 2 to 16 weight percent (wt%) (or 0.034–0.13 volumetric fraction, v/v) of CB were prepared using an ultrasonic shaking bath ( $23^\circ\text{C}$ ) at the same initial relative viscosity ( $2.6 \pm 0.05$ ) of the polymer solutions, using THF as a solvent. A general procedure is described for a poly(styrene)-based composite [61]. Polymer was dissolved in the necessary volume of THF until

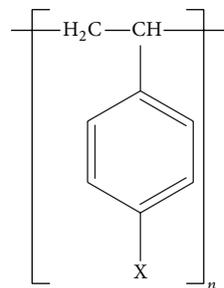


FIGURE 1: Polymer structures and acronyms. Poly(styrene): PS, with  $X = \text{H}$ ; 4-methyl-poly(styrene): 4MePS, with  $X = \text{CH}_3$ ; 4-chloro-poly(styrene): 4ClPS, with  $X = \text{Cl}$ ; and 4-bromo-poly(styrene): 4BrPS, with  $X = \text{Br}$ .

it achieves the mentioned viscosity and it was sonicated, using an ultrasonic processor Ultrasonik 28X (50/60 Hz), until the polymer was completely dissolved; it takes around 30 min. After the polymer is dissolved, the appropriate quantity of CB is added gradually without interrupting the sonication. It takes between 6 and 9 h, depending on the amount of CB: 2–4 wt% (6 hr), 5–7 wt% (7 h), 8–10 wt% (8 h), and higher than 10 wt% (9 h). The THF solvent was evaporated by distillation under reduced pressure. The composite was well dried under vacuum for 24 h. The electrical resistance of the composites was evaluated and resistivity was calculated in order to build the percolation curves. Composites were prepared by triplicate and the specimens were processed for electrical characterization. Finally, percolation threshold was numerically computed by fitting experimental data according to (1).

### 2.4. Polymer and Composite Characterization

**2.4.1. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).** Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out simultaneously using a SDT Q600 modulus from TA Instruments, under nitrogen atmosphere, a heating rate of  $10^\circ\text{C}/\text{min}$ , from 30 to  $600^\circ\text{C}$ . Glass transition temperature,  $T_g$ , and decomposition temperature or temperature at which the polymer lost 10% of its weight,  $T_{10}$ , were obtained, respectively.

**2.4.2. The Weight-Average Molecular Weight ( $M_w$ ) and Polydispersity Index ( $I$ ).** A GPC Agilent 100 Series was used in order to obtain the weight molecular mass and the polydispersity, using a Zorbax Eclipse XBD-C8 column  $150 \times 4.6 \text{ mm}$  of internal diameter at  $60^\circ\text{C}$ , a flux of  $1.6 \text{ mL}/\text{min}$ , and HPLC THF as solvent.

**2.4.3. Density.** Polymer density was measured by two techniques: by direct relationship of mass/volume which in turns was measured for pure polymer cylinders prepared by thermocompression molding. And the second method was by the displacement of water in a calibrated probe at  $23^\circ\text{C}$ . The measurements were very close and their average was taken.

TABLE 1: Thermal, mass, and electronic properties of polymers.

Characterization	Property	Polymer			
		PS	4MePS	4BrPS	4ClPS
Thermal	$T_g/^\circ\text{C}$	106	115	136	131
	$T_{10}/^\circ\text{C}$	385	370	387	382
GPC	Mass of the repetitive unit	80	118	182.9	138.5
	$M_w \times 10^5$ g/mol	1.43	2.45	2.55	2.48
	PD	1,788	2,076	1,394	1,791
	$I$	2.024	1.506	1.370	1.452
Electric	Pauling electronegativity of the 4-substituent	2.1	2.4	2.8	3.2
	magnitude of dipole moment (D) <sup>a</sup>	0.25	0.084	1.45	1.38
	Dielectric constant (17°C, 850 MHz)	2.60	2.43	2.82	2.77

<sup>a</sup>Calculated by MOPAC PM3.

**2.4.4. Relative Viscosity.** The initial viscosity of the polymer solutions used for dispersing CB particles was measured using an Ostwald capillary viscometer previously calibrated with water at 23°C, and then the pure solvent (THF) was measured and finally the polymer solutions. As mentioned before, the initial viscosity of the polymer solution for each composite preparation was  $2.3 \pm 0.05$ .

**2.4.5. Dielectric Constant.** Pure polymers were molded to disks of 2 cm diameter  $\times$  0.9–1.1 mm thickness by compression molding. A steel mold was heated at 10°C above polymer's  $T_g$ , it was filled with the polymer cut in small pieces, and a pressure of 12 Kg/cm<sup>2</sup> was applied for 30 min. Then, the mold was cooled down to 60°C, mechanical compression was removed, and sample was cooled at room temperature (23°C). The dimensions of the transparent plates were measured with a micrometer and then the dielectric constant was evaluated. Polymer dielectric constant was measured using an Agilent 4991A RF Impedance/Material Analyzer at 850 MHz of frequency range from 17°C to five degrees below the corresponding polymer matrix  $T_g$  into a controllable oven. The dielectric constant ( $\kappa$ ) was calculated by the formula of a parallel plate capacitor as  $\kappa = Ct/\epsilon_0 A$ , where  $C$  is the capacitance of the capacitor,  $\epsilon_0$  is the vacuum dielectric permittivity,  $A$  is the area of the electrode, and  $t$  is the thickness of the capacitor.

**2.4.6. Resistivity Measurements.** Cylinder shaped samples of 1  $\times$  1 cm were prepared by thermomechanical molding from all polymers and composites. 1 g of sample was introduced into a steel mold heated from room temperature to ten grades up to polymer's  $T_g$ , and it was pressed at 12 Kg/cm<sup>2</sup>. The heating was made at a rate of 10°C/min. Finally, molding system was cooled with air to 50°C, pressure was released, and the sample was removed [61, 62]. Resistivity measurements were made with an electrometer Keithley 6517A following the methodology pointed out in [56, 61, 62]. For each composition, the plotted resistivity is the average of nine samples, obtaining a deviation standard of 3% for the conductive zone and 10% for the percolation zone in the percolation curve.

**2.4.7. Percolation Threshold.** For determination of the percolation threshold, numerical fit was carried out on Origin 6 software according to (1). For all cases, three free parameters  $\rho_0$ ,  $X_c$ , and  $\beta$  were considered, where  $\rho_0$  is the proportionality constant. 0.99 of data correlation were reached for running numerical interactions. Best fitting curves were obtained for  $\beta$  very close to 2, and then  $\beta$  was fixed to this value and numerical interactions were run again. The value of the critical exponent agrees with the universal values for 3D media [9].

### 3. Results and Discussion

Thermal properties as  $T_g$  and decomposition of the polymers were evaluated by DSC and TGA, respectively, and they are shown in Table 1. The decomposition temperature of polymers is higher than 380°C for the PS and the halogenated ones. However, 4-methyl-poly(styrene) (4MePS) shows a lower decomposition temperature probably due to the benzyl hydrogen of the CH<sub>3</sub> substituent. These hydrogens need lower energy to break and build up resonance-stabilized species with the aromatic ring. DSC and TGA analyses were a reference to establish the processing conditions of the polymers. There is a large range of temperature between  $T_g$  and  $T_{10}$ , giving us a broad range of work above the  $T_g$  without the decomposition of the polymer.

The weight-average molecular weight ( $M_w$ ) and polydispersity ( $I$ ) were evaluated by GPC. The results are shown in Table 1. It was important to minimize the parameters that could affect the threshold percolation of the studied polymers. As it is shown in Table 1, 4MePS, 4-bromo-poly(styrene) (4BrPS), and 4-chloro-poly(styrene) (4ClPS) have differences in  $M_w$  less than 10,000 g/mol and a polydispersity less than 1.5, with polystyrene (PS) being an exception to this. PS has a different  $M_w$  by 100,000 g/mol compared to the other polymers and a lightly higher dispersion. However, by calculating the polymerization degree (PD), we notice that PS and 4ClPS have almost the same value (1,790), followed by 4MePS with approximately 2,000 repetitive units and finally 4BrPS with only 1,400 units, approximately. If these results had a relevant incidence on the percolation threshold,

we could anticipate that PS and 4BrPS would have the lowest percolation threshold because 4BrPS has the smallest polymer chains and PS has both, the smallest and the largest chains, as indicated by its dispersion.

To avoid the side effects on the percolation threshold, one initial solution viscosity for each polymer ( $2.3 \pm 0.05$ ) was established for preparing the respective composites using THF as a solvent and  $23^\circ\text{C}$  temperature. Such viscosity requires preparing polymer solutions with the following concentrations: PS: 6 g/mL, 4MePS: 8 g/mL, 4BrPS: 5 g/mL, and 4ClPS: 4 g/mL. Obviously, this viscosity is lightly modified by the CB incorporation, but it was compensated with the shaking time. For preparing the polymer composites at the volume fraction of CB, it was necessary to evaluate the polymer density. The average results of the two mentioned methods are PS:  $1.048\text{ g/cm}^3$ , 4MePS:  $1.015\text{ g/cm}^3$ , 4BrPS:  $1.53\text{ g/cm}^3$ , and 4ClPS:  $1.22\text{ g/cm}^3$  and are according to the values published in other sources [63–65].

Pauli electronegativity of the 4-bonded atoms is shown in Table 1, calculus of the magnitude of the dipole moment was made numerically using MOPAC PM3 software, and the dielectric constant is taken at  $17^\circ\text{C}$ . As it is shown, the dipole moment is 0.25 D for PS due to the ethyl group regarded as the equivalent of the polymer's backbone. This group is an inductor electronic donor, meaning that the electronic density is displaced from the backbone chain to the aromatic ring, producing a small dipole moment. When the hydrogen in position 4 from the main chain is replaced by a methyl ( $\text{CH}_3$ ) group, the dipole moment decreases almost to zero. This dipole moment reduction is produced because both groups on the benzene ring (ethyl and methyl) have the same inductor electronic effect in such a way that the vector of dipole moment is almost canceled (0.084 D). The opposite and higher change in dipole moment is observed when a halogen atom is sited in the same 4-aromatic ring position. From a microscopic point of view, the dipole moment (Table 1) has no direct correlation with the electronegativity of those atoms. We expected that 4ClPS had a higher dipole moment than 4BrPs due to its higher electronegativity, even though this is not the only factor that affects it. From a macroscopic view, the dielectric constant ( $\kappa$ ) at  $17^\circ\text{C}$  and 850 MHz only reflects a partial dipole orientation of the polar repetitive units due to the dipole movement that is restricted by the glassy state, whose temperature ( $17^\circ\text{C}$ ) is lower than the corresponding  $T_g$ . However, it shows a difference in polarity at this temperature, the least polar polymer being the 4MePS ( $\kappa = 2.44$ ) and the most one the 4BrPS ( $\kappa = 2.82$ ) and very close one the 4ClPS ( $\kappa = 2.77$ ).

The dielectric properties of a polymer are determined by the charge distribution and also by statistical thermal motion of its polar groups. The dipole units cannot orient themselves below the  $T_g$ ; however, as the temperature increases, the orientation of dipoles is ameliorated, increasing the dielectric constant. Dielectric constant was also evaluated at some predetermined temperatures:  $17^\circ\text{C}$  (as the initial),  $70^\circ\text{C}$ ,  $90^\circ\text{C}$ , and  $100^\circ\text{C}$ , for PS. However, 4MePS was increased to  $105^\circ\text{C}$ , 4ClPS to  $120^\circ\text{C}$  and  $125^\circ\text{C}$ , and 4BrPS to  $130^\circ\text{C}$ . The upper limit for those temperatures was five degrees below

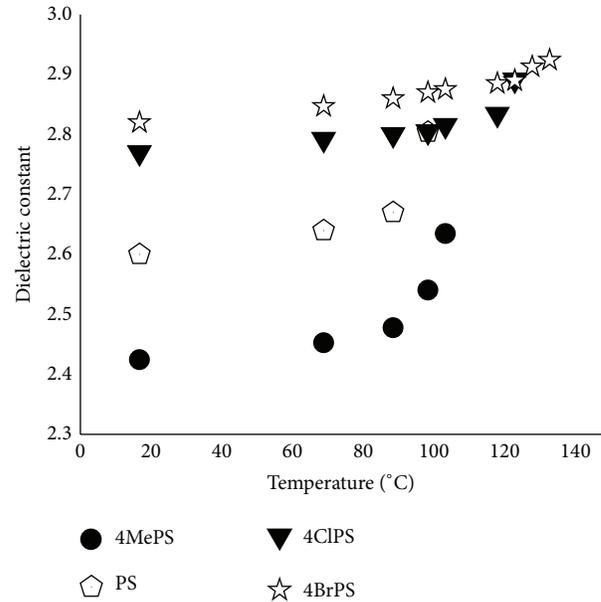


FIGURE 2: Dielectric behavior of polymers related to temperature.

the corresponding  $T_g$ 's. The dielectric constant behavior with respect to temperature is plotted in Figure 2. As we can see, the dielectric constant of PS and 4MePS increases with temperature. At  $100^\circ\text{C}$ , PS and 4ClPS have the same dielectric constant, but PS has reached its maximum (an increase of 7%). 4MePS increases by 6.5% from its initial value. Although 4ClPS shows the same tendency of increasing the dielectric constant with temperature, the increasing percentage is not as high as that for PS; it only increases by 4.2% reaching 4BrPS at its maximum. 4BrPS presents the less important increase of dielectric constant; it remains almost constant with changing temperature (3.2%). 4BrPS resulted to be the less "orientable" polymer maybe due to the heavy repetitive unit.

The polymer composites were prepared as described; polymer and CB aforesaid densities were taken into account for the composition calculus. Results of electrical resistivity depending on CB in wt% and fraction volume,  $v/v$ , for each composite are plotted in Figure 3. The corresponding values of the percolation threshold and the dielectric constant are listed in Table 2. A critical exponent of  $\beta = 2$  (Figure 3) was obtained for resistivity as a function of the volumetric fraction, while the numerical fit of the percolation curves in terms of the wt% CB rendered a  $\beta = 2.3$  value. These values indicate that percolation networks are interconnected giving a 3D-fractal structure, which is consistent with the used percolation model (1).

On the other hand, a decrease of the percolation threshold is an evidence that it is linked to the polymer polar nature. A decrease in the percolation threshold means the construction of conductive networks with low concentration of carbon particles due to their good disaggregation and distribution through the entire polymer matrix. The carbon black agglomeration renders an increase in the percolation threshold and a secondary effect as follows: at concentrations higher than

TABLE 2: Analysis of the percolation threshold related to the dielectric constant measured between 17°C and 5°C below the corresponding polymer  $T_g$ .

Polymer	Percolation threshold v/v CB	Percolation threshold wt% CB	Dielectric constant (17°C, 850 MHz)	Dielectric constant ( $T_g - 5^\circ\text{C}$ , 850 MHz)
4MePS	0.058	9.4	2.43	2.64
PS	0.054	8.9	2.60	2.80
4ClPS	0.047	6.9	2.77	2.89
4BrPS	0.051	5.9	2.82	2.92

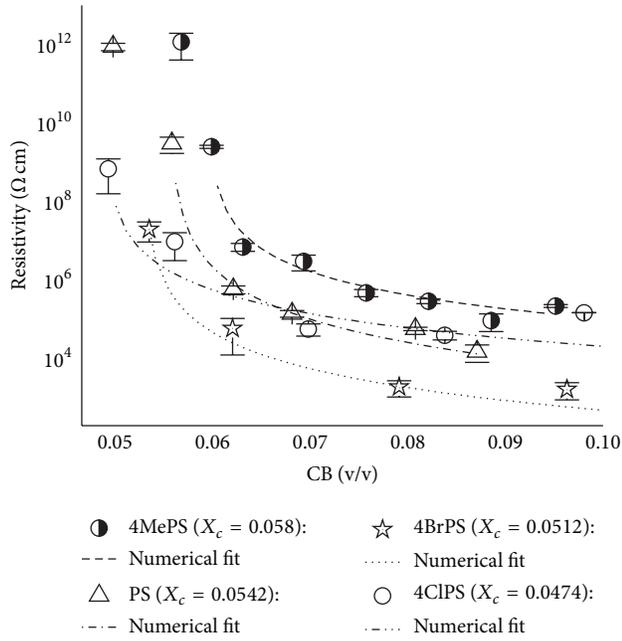


FIGURE 3: Electrical resistivity of composites as a function of carbon black volume fraction.

percolation threshold, it could be noticed that the changes in resistivity related to the CB concentration (Figure 3) also depend on the chemical nature of the polymer matrix.

As the carbon particles used for composite preparation were the same, it should be expected that the resistivity of each compound converges in the same limit value independent of the polymer matrix at CB concentrations higher than percolation threshold. However, the maximum resistivity reached has different value for each composite, as it is shown in Figure 3. For 4MePS, the maximum resistivity is in the order of 10<sup>6</sup> Ω·cm, whereas, for 4ClPS composites, it is barely 10<sup>3</sup> Ω·cm, which is a difference of 3 orders of magnitude. Above the percolation threshold, the conductive networks are interconnected among them. This interconnection could be modified if the CB disaggregation and dispersion are not homogeneous, producing agglomeration of the particles. A better distribution of the carbon black particles could allow a superior interconnection between the different chains of the same CB filler fraction in such a way that the composite reaches a lower electrical resistivity. The polymer matrix role is relevant because, for the same carbon black particle

composition, there is a great difference in the resistivity values, as shown in Figure 3. Therefore, the critical parameter values suggest the three-dimensional conductive chains in all the studied polymer matrixes due to the dipolar moment of the lateral groups on the backbone, in such a way that the presence of polar groups facilitates the CB dispersion, the building of electrical networks, and the faster achievement of the percolation threshold. These results match the qualitative observations made by [39], in which the polar side groups have an influence on the preferential construction of conductive networks.

The behavior of percolation threshold related to the polymer dielectric constant in weight percent and volume fraction is shown in Figure 4. The difference in dielectric constant at 17°C is very subtle between PS-4MePS and 4ClPS-4BrPS. However, we can appreciate that a real difference in the percolation threshold exists. A clear tendency in diminishing the percolation threshold as the dielectric constant of the polymer increases is shown in the wt% CB curves. However, when the CB volume fraction is calculated, the 4BrPS did not render the lowest percolation. Maybe the high density of this polymer makes CB particles get more volume than 4ClPS. Despite this unpredicted behavior, the tendency seems to be the same: both polymers with the highest dielectric constant also produce the formation of CB composites with less percolation concentration.

Those behaviors are the evidence that an asymmetric electronic density has an important effect on favoring the dispersion and distribution of the CB particles, having as a consequence a lower percolation threshold. An increase in the polymer dielectric constant results in a decrease of the percolation threshold. Curves of  $M_w$ , PD, and  $I$  versus percolation threshold do not show a similar behavior as the dielectric constant versus percolation threshold. In the extreme cases, for 4MePS, the percolation concentration,  $X_c$ , was calculated at 9.4 wt% CB (0.0584 v/v) and, for 4BrPS, it was 5.9 wt% CB (0.051 v/v CB). This is an important difference since, at molecular level, the chemical structure of both polymers is different only by the presence of a halogen atom or a methyl group into the 4-position of the aromatic ring. For each repetitive unit in 4MePS, the dipole moment is only 0.084 D, whereas, for 4BrPS, it is 1.45 D, the substantial difference which is reflected in the percolation threshold. At a macroscopic scale, the dielectric constant also increases by the presence of the halogen atom being only 2.42 for 4MePS and 2.82 for 4BrPS. The dielectric constant measured below  $T_g$ , at which no orientation order is achieved and being only the atomic polarization that contributes to this dielectric

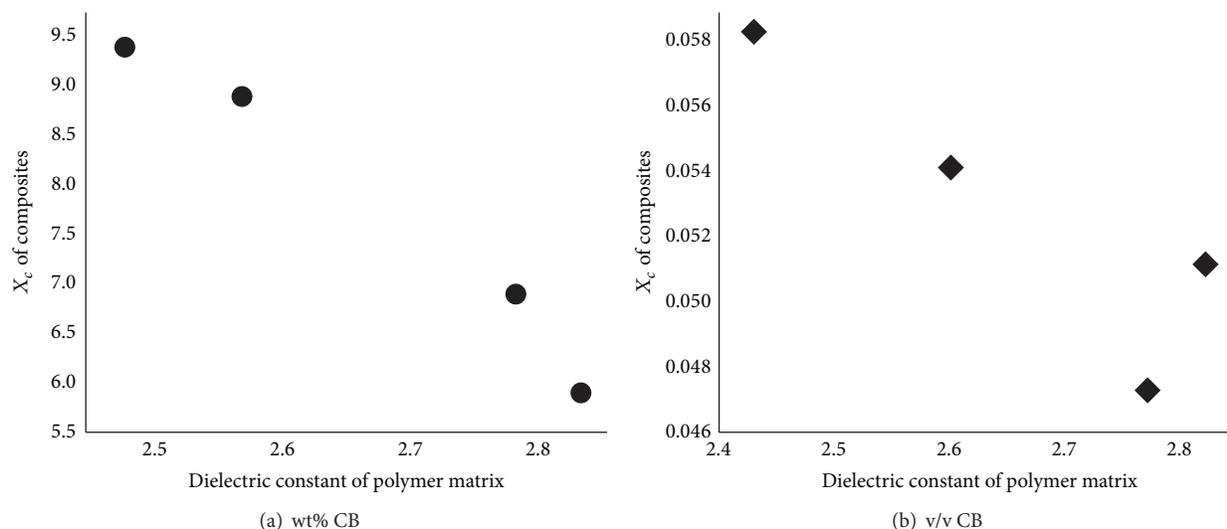


FIGURE 4: Dielectric constant versus percolation threshold in (a) wt% CB and (b) volume fraction CB.

constant, evidences the effect of the substituent atom nature on the aromatic ring.

For explaining such results, the fact that the presence of a dipole moment generated by the presence of electronegative atoms or acceptor functional groups on the polymer is important in order to achieve a good dispersion of the CB particles by creating a better interaction between the groups of the carbon particles and the polar moieties of the main polymer chain could be considered. Then, electrostatic interaction between total electronegative species and carbon black particles is very important while sonication procedure is carried out. Composites were obtained by dissolution method. In this stage, interactions between chains can be depreciated and the mobility is higher than that in the rubber state. Consequently, interaction among CB particles and the repetitive units produce a better disaggregation and distribution of carbon particles. In others words, an appropriate growth of the interconnection of the percolation paths by preferential distribution of the carbon particles in that type of polymers is possible. According to the numerical approximations of CB polymer composites based on PS, 4MePS, 4ClPS, and 4BrPS, high structure percolation chains are built. However, clear effects on percolation threshold are evident for the chemical modified polymer matrix. This is an evidence that there are electrostatic interactions between CB particles and the polar groups on the main polymer chain that promote a much better setting up of the conduction networks as the polarity (dielectric constant) of the polar matrix increases, having as a result a low electric percolation threshold.

#### 4. Conclusions

According to the results, it was proved that a polymer with a dipole moment in the repetitive units has a determinant effect on the percolation threshold. It produces a decrease of the percolation threshold since an asymmetric electronic

density produces a disaggregation and preferential dispersion of the CB particles in order to achieve the network conductive paths with less CB particles. At a macroscopic level, the subtle differences of the dielectric constant at room temperature by the presence of atoms with different electronegativity on the aromatic ring encourage the hypothesis that an increase in the dielectric constant results in a decrease of the percolation threshold. This demonstrates the relevance of the electronic nature of both, polymer and conductive particles, if we want to control the percolation threshold. Electronic nature of polymer, evaluated as dielectric constant, offers the possibility to use this property in the new design of conductive polymer composites. Of course, there is an implication between the chemical nature of the polymer and other properties like the mechanical and thermal ones, which is important to take into account for a potential application.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

#### Acknowledgment

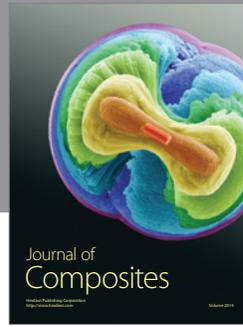
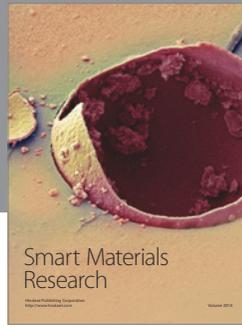
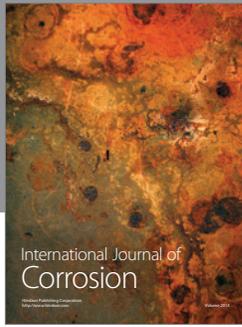
The authors are grateful to the support provided by PRODEP-SEP 2015 “Red de Compuestos Poliméricos, Propiedades y Aplicaciones” Project.

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