Composites of phenolic resin with expanded graphite and conductive carbon black

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Abstract

The phenolic resin (PR) is widely studied as matrix for composites due to its promising mechanical properties and chemical stability. However, which regard to electrical conduction, PR is a typical insulator (electrical conductivity around 10^{-12} S.cm^{-1}), limiting its utilization for electric conduction' applications. Expanded graphite (EG) and conductive carbon black (CB) are fillers that have been utilized to increase the electrical conductivity of several polymers, but they have not yet been enough studied to composites materials with PR. Thus, this study aims at asses to produce composites of PR and EG or CB (2% w / w) and verify the influence these fillers on the composites' electrical properties. The composites were analyzed by FT-IR (Fourier Transform-Infrared Spectroscopy), Impedance Spectroscopy (IS) and Scanning Electron Microscopy (SEM). It was verified that the electric conductivity of the PRs increased due to fillers. The composite PR/CB showed electric conductivity about five orders of magnitude higher than the PR. On the other hand, the composite PR/EG showed greatest electrical conductivity, about seven orders of magnitude higher than the PR (1.1 10^{-5} S.cm^{-1}). These results have shown the efficacy of those fillers in the increase of the electrical conduction in PR-based composites. Therefore, these composites materials have potential to be used as Electromagnetic Interference (EMI) shielding and electrostatic discharge (ESD).

Keywords: Phenolic resin, graphite, carbon black, electrical conductivity.

Introduction

The phenolic resins (PR) are usually obtained by reaction of phenol and formaldehyde, applying or not a cure agent or heating [1]–[3]. There are basically two reaction mediums: i) acid medium, containing excessive amounts of phenol, called novolac resin (reaction with two stages); ii) basic medium, containing excess of formaldehyde, called resol resin (reaction with one stage) [4]–[7]. However, the novolac resin can also be obtained utilizing an excess of formaldehyde [3].

Novalac resins with acid catalysts can be cured by paraformaldehyde, in this case the excess of formaldehyde can act as a curing agent[2]. The reaction in this case occurs in two stages: the first one is represented by the protonation of the carbonyl group of the formaldehyde [8]. In the second stage, it occurs an electrophilic aromatic substitution of phenol at the positions *ortho* and *para* [9]–[11]. After that, a low molecular weight linear polymer is constituted through methylene bridges [12]–[14]. Then, the acid catalyst induces the linkages *ortho-para* and *para-para* [9]. In addition, there are different reactivities of the phenol and methylolated phenols. Their differences in the methylolated phenols depend on whether formaldehyde is present or absent[3].

Several acid catalysts can be used to synthesize the phenol-formaldehyde resins [9]. Among them, strong and weak acids – sulfuric and oxalic respectively – are ones of the most common [11]. The use of oxalic acid as the reaction catalyst has become remarkable due to its relative low sublimation temperature (157 ° C under ambient pressure) compared to other acids. Besides, the oxalic acid completely decomposes into carbon monoxide, carbon dioxide and water for temperatures over than 180°C [1], [11]. Hence, there is no necessity of acid removal from the reaction medium at the end of the cure process. In addition, the one is much less corrosive to the equipment's metal parts compared to strong acids [1].

Polymers in general are insulator materials; usually their electrical conductivity are less than 10^{-12} S.cm^{-1} [15]. The addition of conductive fillers in the polymeric matrix as graphite or MWCNT (multiwalled carbon nanotubes) can increase the composite's electric conductivity many orders of magnitude [16], [17]. By means of that combination, composites have been produced to be used in antistatics, Electrostatic Discharge – ESD applications, among others [18] . Numerous levels of electrical conductivity can be achieved by changing the proportion and type of filler, offering processing flexibility for electronic devices with specific properties [19][20].

The polymers are basically divided into general groups according to their electrical conductivity. Between 10^{-6}–10^{-11} S.cm^{-1}, they are considered low-voltage conductors [21], [22], usually applied as varistors, transistors and bilayered dielectrics[23]. Between 10^{-2} – 10^{-6} S.cm^{-1}, they are classified as semiconductors, which are suitable for Electromagnetic Interference – EMI shielding and Electrostatic Discharge – ESD [24]. Lastly, for values of resistivity below than 10^{-2} S.cm^{-1}, they are classified as conductive polymers, which are applied to heaters, sensors and electric conductors [21], [22] .

About ninety percent of the ESD products use the CB, but other fillers also can be used [25]. The percolation values depend mainly of three factors: type of filler; its shape and its interface with the matrix. The electrical responses of the carbon black–based composites are particularly dependent of the fillers' size, amount and structure [11] [12] .

The difference between carbon black and graphite is based on the layers arrangement; both are built of large sheets of hexagonal rings formed by carbon atoms [26]. For the first one, the carbon sheets are separated of each other with the distance of 0.142nm.The second one is characterized by a tri-dimensional order with distance of 0.335 nm [16]. Graphite is used for products that require conductivity, besides lubricating coatings and flame retardant [22], [27].

In this study, it was evaluated the impacts of carbon black and expanded graphite on the electronic conduction of phenolic resin–based composites. For that, the composites' physicochemical features were evaluated by the FT-IR technique; the fillers and composites morphologies were evaluated by SEM and the electric responses were assessed by the IS technique.

Experimental

The **Table 1** shows the nomenclatures utilized for the samples assessed in this study.

Table 1. Compositions and nomenclatures of the samples.

Composition	**Nomenclature**
Phenolic resin neat	PR
Phenolic resin with carbon black	PR/CB
Phenolic resin with expanded graphite	PR/EG

The synthesis of the samples started through the preparation of a mixture of 33% (mol) of phenol and formaldehyde. The phenol (99%, Labsynth) and formaldehyde (37%, Labsynth) were vigorously stirred for 30 minutes in an aqueous medium. Then, acid oxalic was added into the reaction medium as the acid catalyst (2:3 w / w based on formaldehyde). The solution was stirred for 90 minutes; sequentially heated to 75˚C and stirred for 20 minutes at this temperature, intending to increase the solution's viscosity without boiling the water. After that, all the samples formed biphasic systems (aqueous phase supernatant and organic phase). The organic phase was isolated for each sample and received the fillers.

The fillers were added at 2% w / w in relation to phenol. Super conductive carbon black (Printex XE2B Beads) by the Orion Engineered Carbons GmbH; and expanded graphite (HC11) produced by Nacional de Grafite Ltda were utilized as fillers.

A high energy mixer was used to homogenize the samples, including the resin neat. For that, it was utilized the Vortex equipment at 2003 rpm for 30s. The curing procedures followed the stages: 80 ºC/2 hours, 100 ºC/30 minutes and 170 ºC/1 hour (heating rate of 3 ºC.min^{-1}) using alumina crucibles.

The samples were characterized by FT-IR using the Attenuated Total Reflectance technique – ATR, in the Agilent Technologies Cary 630 spectrophotometer. The analyzes were processed between 650 and 4000 cm^{-1}, resolution of 4 cm^{-1} and 64 accumulations.

The fillers and composites morphologies were observed by means of the Magellan 400L SEM equipment, operating at 25kV. For that, the composites had suffered cryogenic fracture and their surfaces were then covered with gold by sputtering before the analyzes.

Impedance Spectroscopy analyzes were realized in duplicate by the Solartron SI 1260 Impedance Analyzer coupled to the Solartron 1296 dielectric interface. As electrode, an alloy of gold-palladium was sputtered for 300 seconds in both sides of the samples. The analyzes were performed from1 MHz to 500 mHz at room temperature (25° C). For data analyzes, it was used the ZView software. As a complementary analysis, the High Resistance Meter HP 4339B with a Resistivity Cell HP 16008B was used to measure the electrical conduction of the highly insulator samples.

Results and discussion

The **Fig. 1** shows the structural characterization of the samples. The spectra are quite similar, in which characteristic bands for the phenolic resin appeared for the sample neat and phenolic resin–based composites.

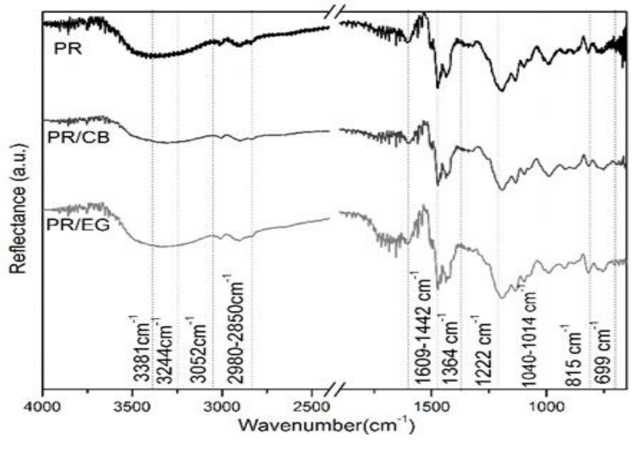

Fig. 1. FT-IR spectra phenolic resin neat and phenolic resin-based composites.

The broad band at 3244cm^{-1} is attributed to O–H axial deformation [28]; whereas the molecular hydrogen bond appears around 3381cm^{-1}. The band around 3052cm^{-1} is related to axial deformation of aromatic C–H [28]. The region between 2980–2850 cm^{-1} presents the aliphatic hydrogen stretching for bonds of CH_2 as a series of low intensity peaks [29], [30]. The bands at around 1609, 1498, 1476 cm^{-1} are related to axial deformation of C=C rings [28] and the bands around 1468, 1452, 1442cm^{-1} are attributed to angular deformation of C–H. The band at 1364cm^{-1} refers to the angular deformation in the plane of O–H; whereas the band around 1222cm^{-1} is related to axial deformation C–O.

The absence of bands around 1040, 1023, 1014cm^{-1}, attributed to the axial deformation of C–O in case of primary alcohols [28], is characteristic of modified novolac resins [1]. The bands at 815 cm^{-1} and 753 cm^{-1} are related to angular deformation out-of-plane for C=C rings [28]; and the band 699 cm^{-1} is attributed to the angular deformation out-of-plane of C=C ring [28].

The SEM images of resin neat, composites and their respective fillers are presented in the **Fig. 2**. The resin and composites contain pores due to the water elimination, which is formed as subproduct of the synthesis stage. The fillers present different sizes and shapes. The particles of carbon black **(Fig. 2C)** are arranged in dense agglomerates with sizes over than 200 μm. On the other hand, expanded graphite apparently shows soft agglomerates with sizes close to 50μm, composed by particles in submicrometric/ nanometric scale. These differences may impact on the efficacy of the fillers dispersion into the phenolic resin matrix, impacting the electrical percolation by consequence.

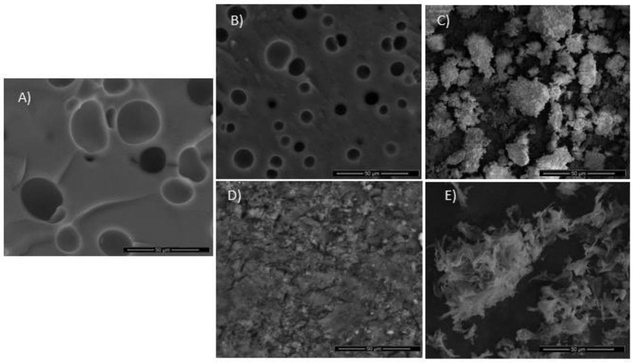

Fig. 2. SEM images at magnification of two thousand times: A) PR; B) PR/CB; C) CB (filler); D) PR/EG; E) EG (filler).

The **Fig. 3** presents the results of electrical characterization for the samples. The **Fig. 3 (A)** presents the complex impedance formalism (Nyquist plot). It is noteworthy that the resistivity differed in several orders of magnitude. The sample neat showed resistivity higher than 10^{12} Ω.cm; thus, its semicircle could not be observed in the complex plane.

Since the samples results were quite different, aiming a better visualization, the **Fig. 3 (B)** presents the impedance modulus *versus* the logarithm of applied electric field.

Thereby, the **Fig. 3 (B)** shows that the impedance modulus indefinitely increases when the frequency of electric field decreases for the phenolic resin neat. It is justified due to the insulator nature of phenolic resins. Thus, since the RP resistivity overcame the capacity of measurement by the impedance technique, a resistivimeter was utilized. The resistivity estimated was 10^{12}, which confirms the high insulator nature of the phenolic resin neat.

On the other hand, the samples PR/CB and PR/EG presented a significant reduction on the electrical resistivity when compared to the PR. The sample with expanded graphite particularly showed the best results of electric conduction. It can be explained by the fillers sizes and morphology. The expanded graphite has shown soft agglomerates, apparently composed by submicrometer/ nanometric particles. It can lead to a better dispersion throughout the phenolic resin matrix. This fact highly favors the contact between the particles and the electric percolation, by consequence. On the other hand, the carbon black has presented dense agglomerates, which could limit the filler dispersion in the phenolic resin matrix, impacting in a less increment in the electronic conductivity

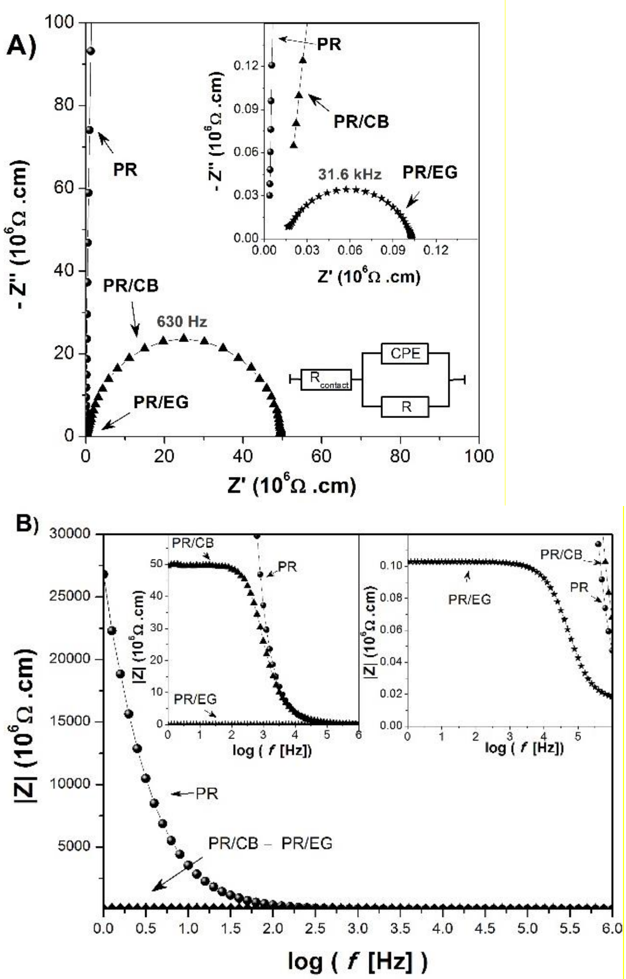

Fig. 3. Complex Impedance formalism: A) Nyquist plot; B) Impedance Modulus *versus* the logarithm of applied electric field.

The **Table 2** shows the results of fitting of the experimental data to the equivalent circuit (presented in **Fig. 3-A**). In this table, β represents the depression angle; C the capacitance; ρ the resistivity; σ the conductivity and f_0 the relaxation frequency.

Table 2. Electrical Properties of phenolic resin neat and phenolic resin-based composites.

Samples	β-CPE (degree)	C (F)	ρ (Ω.cm)	σ (S.cm^{-1})	f_0 (Hz)
PR	–	–	10^{12}	10^{-12}	–
PR/CB	4.2	6.2 10^{-12}	4.9 10^{7}	2.0 10^{-8}	630
PR/EG	13.3	6.7 10^{-11}	9.0 10^{4}	1.1 10^{-5}	3.2 10^{4}

Therefore, these results corroborate with the previous discussion. The PR presented conductivity less than 10^{-12}S.cm^{-1}, which is expected to resins in general. Values of β indicates that PR/CB is less electronically inhomogeneous than PR/EG, which can be a consequence of structure, chemical inhomogeneity and morphology of the fillers.

The capacitance of PR/EG was close to ten times higher than PR/CB. It can be explained due to the fillers morphology: since EG has a smaller particle size, it is expected that its surface area be much higher than the CB. The capacitance is proportional to the interface area between the particles and resin phenolic matrix, which explain the higher values of capacitance for PR/EG.

Lastly, the sample PR/CB showed electrical conductivity about five orders of magnitude higher than the phenolic resin neat; whereas the sample PR/EG was the one that presented highest conductivity, close to seven orders of magnitude higher than the PR neat.

Conclusion

The phenolic resin was satisfactorily synthesized and the composites could be produced by the insertion of fillers before the cure process. Different values of electrical conductivity were obtained, depending of the type of filler utilized. The carbon black composites showed values close to 5.10^{-7} S.cm, which is promising for materials to be applied in low voltage applications. The sample with expanded graphite was the one that presented the highest electrical conductivity (1.1 10^{-5} S.cm). This sample can be considered as a potential material to be utilized to EMI shielding and ESD. The lower filler agglomeration and particles sizes allowed a greater contact between the conductive particles, leading to an increment in the electrical conductivity.

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Author's contributions

Conceived the plan: CGR; Performed the experiments: CGR, JAD; Data analysis: CGR, JAD; Wrote the paper: CGR, JAD, RB, AAL. Authors have no competing financial interests.

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