EMI Shielding Effectiveness and Dielectrical Properties of SBS/PAni.DBSA Blends: Effect of Blend Preparation

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ABSTRACT: This work investigates the effect of different preparation routes including mechanical mixing and *in situ* polymerization of aniline on the electromagnetic interference shielding effectiveness (EMI SE) over the X-band (8–12 GHz) frequency range for polyaniline doped with dodecylbenzene sulfonic acid (PAni.DBSA) filled in styrene–butadiene–styrene triblock copolymer matrix. The dc conductivity and dielectrical properties were also investigated. For all systems, the electrical conductivity, dielectric constant, and EMI SE increased with the increase in the concentration of PAni.DBSA. Blends prepared by the *in situ* polymerization exhibited higher conductivity and dielectric constant and better EMI SE characteristics than the physical blends with similar amount of PAni.DBSA. EMI SE value as high as −35 dB has been achieved with about 30% of PAni.DBSA prepared by the *in situ* polymerization. Regarding physical blends, those involving PAni.DBSA prepared by a redoping process displayed better EMI SE. For all systems under consideration, the conductivity and EMI SE bear an exponential relationship that can be represented by a master curve. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1476–1485, 2012

Key words: polyaniline; SBS; *in situ* polymerization; dielectric properties; EMI shielding interference

INTRODUCTION

Electromagnetic interference (EMI) is considered a modern environmental pollution because of the development of sophisticated electronic devices for industrial, commercial, and military applications, whose performance is affected by the electric and electronic signals emitted by other equipments.[1] Several studies in the literature have been focused on the development of microwave absorption and shielding materials. Traditionally, the EMI shielding is made by metals because of their high conductivity and dielectric constant. However, they are heavy, have great tendency to corrosion, and present poor processability. Nowadays, the interest on conductive polymeric materials constituted by conductive filler dispersed inside a flexible and processable polymer has been increased significantly because of their lightweight and good processability.[2,3] Among several conductive fillers available, intrinsically conducting polymer (especially polyaniline [PAni]) has been extensively studied because of its good environmental stability in both conductive and insulating forms, excellent physical and chemical properties, and also excellent corrosion resistance.[4] In addition, PAni presents a unique shielding mechanism in the sense that it not only reflects but also absorbs electromagnetic radiations, which is very interesting for military applications.[5,6]

The EMI shielding effectiveness (EMI SE) of PAni-based conducting composites has been evaluated using different insulating matrices such as styrene–butadiene rubber,[7] ethylene–propylene–diene copolymer,[6–8] poly(vinyl alcohol),[9] acrylonitrile–butadiene–styrene copolymer,[10] poly(vinyl chloride),[11] ethylene–vinyl acetate copolymers,[12,13] acrylic polymers,[14,15] polyurethane,[16,17] and silicone rubber.[18,19] Most of these systems use PAni doped especially with protonic acids, which render the conductive form of PAni more compatible with the organic polymers.[20] Despite the use of different dopant approaches, PAni is brittle and contributes for a decrease in mechanical and impact resistance of the corresponding composite because of its rigid structure.[21] The choice of an appropriate insulating

matrix should minimize these drawbacks. In this context, styrene–butadiene–styrene (SBS) block copolymer has been shown to be an efficient matrix for the development of PAni-based conducting polymer composite through melt mixing,[22–24] solution mixing,[25,26] and *in situ* polymerization of aniline in the presence of different amounts of SBS.[24,26–31] The compatibility between PAni and the SBS matrix was enhanced by using dodecylbenzene sulfonic acid (DBSA) as the protonating agent.[22,27]

The method used for the preparation of PAni.DBSA significantly affects the conductivity of the melt-mixed SBS/PAni.DBSA blends. PAni.DBSA prepared by a redoping process resulted in SBS-based blends with higher conductivity values when compared with that prepared by one-step emulsion polymerization.[24,30,31] This behavior was attributed to an additional doping process promoted by the shear forces during mixing with SBS (the thermal doping process) imparted by the presence of molecular DBSA in redoped PAni.DBSA.[7,21] The blends prepared by *in situ* polymerization also display better conductivity and higher dielectric constant than blends prepared by melt mixing because of a favorable morphology characterized by the presence of interconnected microtubules.[24,26,30] However, the crystallinity degree of PAni.DBSA component is lower in the blends prepared by *in situ* polymerization, which was attributed to a better dispersion of PAni.DBSA and an increase of the disorder related to the conducting polymer network.[30]

Recently, the EMI shielding properties of conducting composites involving poly(styrene-*b*-styrene–butadiene-*b*-styrene) (STF) and PAni.DBSA were evaluated by our group.[32] The work revealed that the composition with highest amount of PAni.DBSA presented the highest EMI SE and the highest value of reflection power.

Continuing our studies devoted to SBS/PAni.DBSA conducting blends and to the development of new EMI shielding materials, the aim of this study is to relate the different procedures to prepare PAni.DBSA and their blends with the EMI SE. It is well known that microwave behavior of conducting polymers and composites is critically dependent on dielectrical properties of the material,[33] which in turn depend on the synthetic procedure of the polymer.[34,35] Therefore, the objective of this study is also to determine the dielectrical properties of the composites as a function of frequency and to make a comparison with the EMI SE. For these purposes, SBS/PAni.DBSA blends have been prepared by two different procedures: melt mixing and *in situ* polymerization. The melt-mixing process used PAni.DBSA prepared by two different procedures: redoping process and one-step emulsion polymerization.

EXPERIMENTAL

Materials

Aniline (analytical grade; Merck, Darmstadt, Germany) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS, analytical grade; Merck), chloridric acid (HCl, analytical grade; Merck), and DBSA (technical grade; Pro-Quimil Ltda, São Paulo, Brazil) were used without purification. SBS block copolymer (TR-1061) was kindly supplied by Petroflex Industria e Comercio (Rio de Janeiro, Brazil). The SBS sample presents the following characteristics: PBD content $= 70$ wt %; $M_w = 120,000$.

Synthesis of conductive PAni.DBSA

Redoping process (PAni$_R$)

The synthesis of PAni.DBSA by the redoping process was performed according to the literature procedure[31,36,37] and involved the previous preparation of PAni doped with HCl using APS as an oxidant at 0°C for 3 h, followed by a dedoping process using $0.1M$ aqueous solution of ammonium hydroxide. After the deprotonation process, the emeraldine base (EB) was redoped with DBSA by mixing both components (EB : DBSA $= 1 : 1$ molar ratio) in an agate mortar, according to the procedure adapted from the literature.[21,36] The PAni.DBSA obtained by this method presented a dc electrical conductivity of 4.4 ± 0.3 S/cm.

Emulsion polymerization process (PAni$_{EM}$)

The inverted emulsion polymerization of aniline was carried out according to the procedure described in the literature.[21,24] In a typical polymerization, 16.7 g (0.051 mol) of DBSA and 4.7 mL (0.051 mol) of aniline were dissolved in 250 mL of toluene under stirring. The medium was kept at 0°C, and an aqueous solution containing 11.36 g (0.051 mol) of APS in 40 mL of water was added. After 6 h, the reaction medium was poured into methanol, filtered, washed, and dried. The PAni.DBSA obtained by this method presented a dc electrical conductivity of 0.4 ± 0.2 S/cm.

Preparation of SBS/PAni.DBSA blends

The SBS/PAni.DBSA blends were prepared by mechanical mixing and *in situ* polymerization of aniline in the presence of SBS. The composition of the different SBS/PAni.DBSA blends is listed in Table I.

The mechanical mixing used PAni.DBSA prepared by both redoping process (SPAni$_R$) and inverted emulsion polymerization (SPAni$_{EM}$). Blends of different compositions of SBS/PAni.DBSA were prepared in a Berstoff two-roll mill at 60°C for 10 min. The rolls worked at two speeds: 25 and 20 rpm (back and front roll, respectively). The blends were

Conductive filler	Filler (%)	Method	Code
Redoped polyaniline	5	Mechanical mixing	$SPAni_R05$
	15		$SPAni_R15$
	30		$SPAni_R30$
Polyaniline by emulsion polymerization	5	Mechanical mixing	$SPAni_{EM}05$
	15		$SPAni_{EM}15$
	30		$SPAni_{EM}30$
Polyaniline by emulsion polymerization in the presence of SBS	5	In situ	$SPAni_{IN}05$
	16	In situ	$SPAni_{IN}15$
	32	In situ	$SPAni_{IN}30$

then compression molded at 90°C and 1.0 MPa pressure for 7 min.

The blends prepared by *in situ* polymerization ($SPAni_{IN}$) were prepared by first dissolving different amounts of SBS in toluene. Then, 16.7 g (0.051 mol) of DBSA and 4.7 mL (0.051 mol) of aniline were added. The medium was kept at 0°C, and an aqueous solution containing 11.36 g (0.051 mol) of APS in 40 mL of water was slowly added. After 6 h, the medium was poured into methanol. The precipitate was filtered, washed with methanol, and dried under vacuum at room temperature. The amount of PAni.DBSA formed inside the SBS matrix is slightly different from that prepared by mechanical mixing as indicated in Table I.

Characterization

The dc volume resistivity was measured using a Keithley 6517A electrometer (using two-plate technique according to ASTM D-257 methodology; Keithley Instruments Inc., Cleveland, OH).

The dielectrical properties of different composites were measured using high-precision. LCR meter, model QuadTech 7600, from Agilent Technologies (Santa Clara, CA) over the frequency range 10–10^6 Hz. For these experiments, three electrode systems were used, namely, positive electrode, negative electrode, and guard electrode.

The EMI SE of different composites was measured over X-band microwave frequency range of 7.8–12.4 GHz using scalar network analyzer, Model HP 8757C from Hewlett-Packard (Lake Mary, Florida) coupled with a seep oscillator, Model H.P. 8350D from Hewlett Packard (Lake Mary, Florida), a power splitter, and a detector. A X-band waveguide as the sample holder and samples having 2 mm thickness were used for the measurements. The accuracy in the EMI SE measurements is ±0.5 dB.

EMI shielding theory

Electromagnetic radiation can be divided into near-field and far-field regions.[1,3,38,39] In the near-field region, the electromagnetic signal can be predominantly an electric vector or a magnetic vector depending on the nature of the source. In the far-field region, plane waves exist in which the electric and magnetic vectors have an equal ratio in phase and are orthogonal to each other. The plane radiation (far field) is the most concerned in measuring SE. An electromagnetic shielding material is a material that attenuates the irradiated electromagnetic energy. The SE is a number that quantifies the amount of attenuation typical of a particular material and can be defined as follows:

$$SE = 10 \log(P_{inc}/P_{trans}), \qquad (1)$$

where P_{inc} is the incident power density at a measuring point before shield is in place, and P_{trans} is the transmitted power density at same measuring point after shield is in place.

The reflection loss is defined by the following equation:

$$R = 10 \log(P_{inc}/P_{ref}), \qquad (2)$$

where P_{ref} is the reflected power density at same measuring point.

It is evident that for a lossless material,

$$P_{inc} = P_{ref} + P_{trans} + P_{abs}, \qquad (3)$$

P_{abs} can be quantified as the absorbed power inside the dielectric, and

$$P_{abs} = 1 - P_{trans} - (P_{inc})/(P_{trans}), \qquad (4)$$

where P_{abs} is the power absorbed by a lossy dielectric.

However, EMI is the consequence of reflection loss, transmission or absorption loss, and internal reflection loss at exiting interfaces of the incident electromagnetic waves inside the sample. These three losses are inter-related by

$$S = (R + A + B)dB, \qquad (5)$$

where S is the SE or insertion loss that represents the reduction (expressed in dB) of the level of an electromagnetic field at a point in space after a conductive barrier is inserted between that point and the source; R is the sum of initial reflection losses (in dB) from both surfaces of the shield exclusive of additional reflection losses; A is the absorption or penetration loss (in dB) within the barrier itself; and B is the internal reflection loss at exiting interface (in dB). For plane wave radiation, R and A may also be calculated from the following equations:

$$R = 108 + \log(G/\mu f), \qquad (6)$$

$$A = 1.32t(G\mu f)^{1/2}, \qquad (7)$$

where G is the conductivity of the sample relative to copper, μ is the magnetic permeability of the sample relative to vacuum or copper; f is the frequency of radiation (in MHz); and t is the thickness of the sample (in cm). It is observed from these equations that reflection loss is directly proportional to the log of conductivity and inversely proportional to the permeability of the sample and also to the log frequency of the incident electromagnetic wave. However, absorption loss is directly proportional to the thickness of the sample and square root of frequency, conductivity, and permeability of the sample.

EMI SE is defined and calculated based on the following expression:

$$\text{Sheilding Efficiency}(\%) = \frac{(A + R + B) \times 100}{P_{\text{inc}}}, \qquad (8)$$

where A = absorption loss (expressed in dB); R = reflection loss (in dB); and B = correction factor (in dB; for multiple reflections in thin shields).

RESULTS AND DISCUSSION

Electrical conductivity and morphology

The electrical resistivity values of SBS/PAni.DBSA blends prepared by different procedures are illustrated in Figure 1. The blends prepared by the *in situ* polymerization of aniline displayed lower resistivity values and suggest an insulator–conductor transition at a concentration of PAni.DBSA lower than 5 wt %. According to our previous reports,[24,30] this behavior is attributed to a peculiar morphology
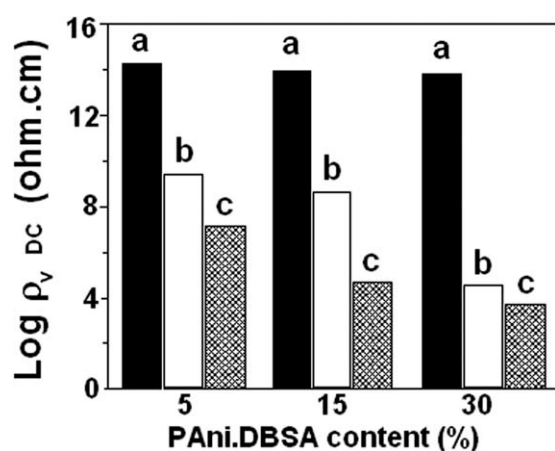

Figure 1 DC electrical resistivity of SBS/PAni.DBSA as a function of composition and preparation procedure: (a) SPAni$_{EM}$, (b) SPAni$_{R}$, and (c) SPAni$_{IN}$ systems.

characterized by the presence of microtubules of PAni.DBSA with large aspect ratio and by the formation of an interconnected conducting network. Regarding the physical blends (mechanical mixing), those which used PAni$_R$ presented lower resistivity values than SPAni$_{EM}$. These results are due to the presence of molecular DBSA in the redoping PAni.DBSA sample, which may impart an additional doping process of the PAni chain caused by the shear forces during melt blending.[7,21]

Dielectrical properties

The complex dielectric constant can be separated into its real part (ε') known as dielectric constant or relative permittivity and its imaginary part (ε'') known as loss factor or dielectric loss.[40] The variation of the dielectric constant (ε') against frequency for different SBS/PAni.DBSA blends is presented in Figure 2. Physical blends related to the SPAni$_{EM}$ series did not present significant changes of dielectric constant with the concentration of PAni.DBSA. For the other series, SPAni$_R$ and SPAni$_{IN}$, the dielectric constant values increased with the concentration of PAni.DBSA at any particular frequency. This behavior is expected because PAni.DBSA is highly polar and the dielectric constant depends on the number of dipole per volume unit of the composite (dipole density).

The dependence of the dielectric constant with the frequency depends on the blend preparation methodology. Blends related to the SPAni$_{EM}$ series did not present any significant change of this property with the frequency, whereas those related to the SPAni$_R$ and SPAni$_{IN}$ displayed a great increase of the dielectric constant at lower frequency. Moreover, for the blends prepared by the *in situ* polymerization (SPAni$_{IN}$ series), the ε' was found to increase almost linearly with the decrease in frequency over the whole range of measurement frequency, and this behavior was observed for all blends regardless the concentration of PAni.DBSA. The decrease in the dielectric constant with the increase in frequency may be ascribed to the effect of the increased contribution of interfacial polarization. The presence of insulating matrix prevents free discharge of charge carriers that are not able to reorient themselves fast enough to respond to applied field.[41] The interfacial polarization generally arises in heterogeneous systems consisting of two or more phases with appreciable difference in dielectric constant and conductivity and is caused by the alternating accumulation of charges at the interface between different phases.[3] SBS/PAni.DBSA blends prepared by the *in situ* polymerization (SPAni$_{IN}$ series) exhibited the highest dielectric constant among the three sets of blends at similar concentration of filler. This behavior may be
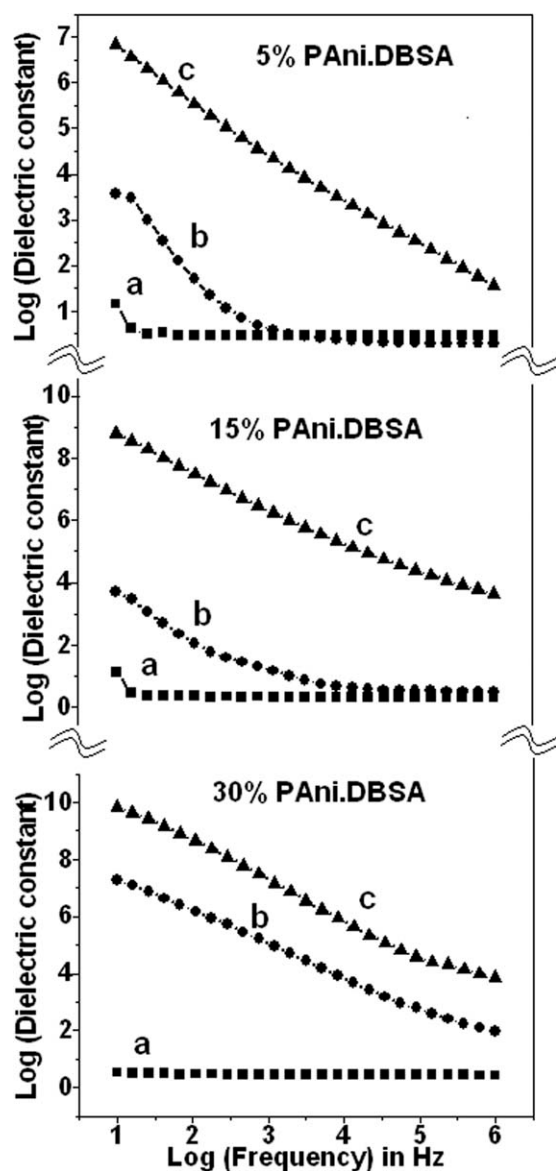
Figure 2 Dependence of dielectric constant (ε') with the frequency for different SBS/PAni.DBSA blends: (a) SPAni$_{EM}$, (b) SPAni$_R$, and (c) SPAni$_{IN}$ systems.

attributed to the highest dispersion and orientation of the PAni.DBSA in these SPAni$_{IN}$ systems, generating an increase of SBS–PAni.DBSA interface that contributes for the increase of accumulation of charge in this region. The increase in dielectric constant at lower frequency may also be to some extent due to electrode potential, as discussed later in the text during explanation of dielectric loss.

The dielectric loss (ε'') versus frequency for the different SBS/PAni.DBSA blends is illustrated in Figure 3 and also varies in similar fashion as that of dielectric constant. For all types of blends, the loss factor at any particular frequency increased with the increase in the concentration of PAni.DBSA. An increase of ε'' was also observed at lower frequency, and this phenomenon is more pronounced in blends

of SPAni$_{IN}$ series. Two different types of polarization are operative in the SBS/PAni.DBSA systems. The first one is the dipolar polarization generally operative at higher frequency region and is related to the presence of highly polar PAni.DBSA. The second type of relaxation is due to the interfacial polarization as these blends are heterogeneous in nature consisting of polar and conducting PAni.DBSA dispersed in the insulating SBS matrix as mentioned earlier. The nature of both dielectric constant and dielectric loss revealed that the effect of both dipolar and interfacial polarization are the maximum in SPAni$_{IN}$ blend series, whereas the effect is intermediate in physical blends of SPAni$_R$ series. All these behaviors are in agreement with the conductivity values discussed above.
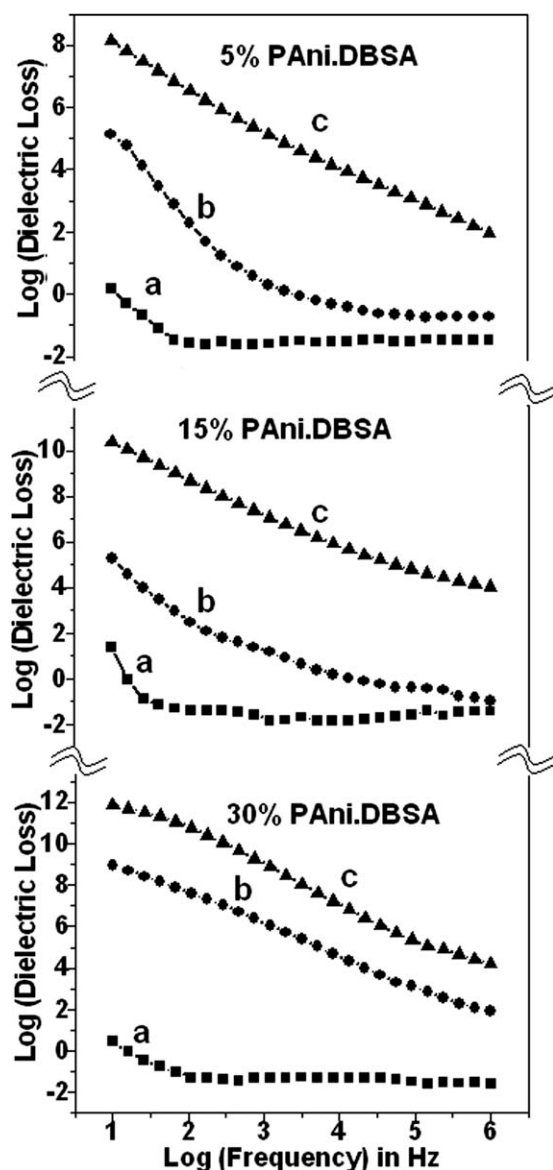

Figure 3 Dependence of dielectric loss (ε'') with the frequency for different SBS/PAni.DBSA blends: (a) SPAni$_{EM}$, (b) SPAni$_R$, and (c) SPAni$_{IN}$ systems.
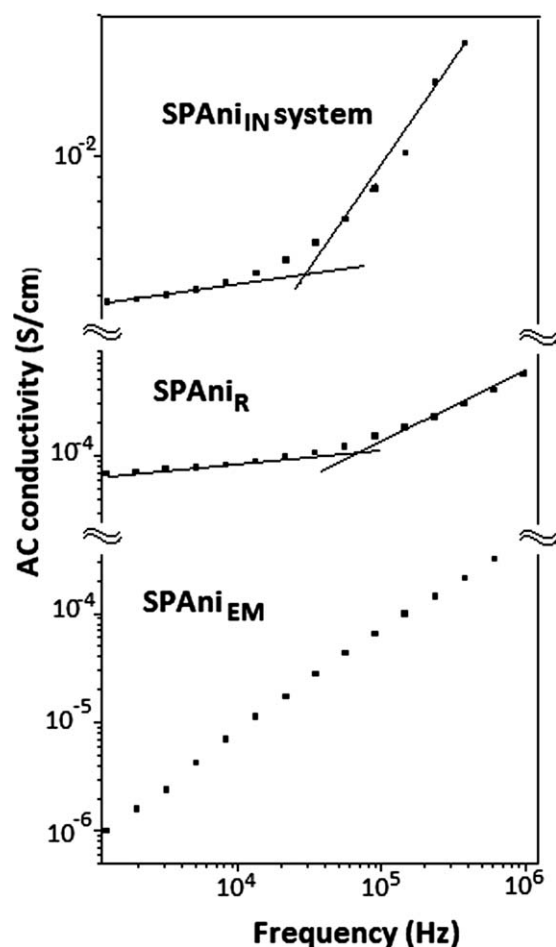
Figure 4 Dependence of ac conductivity (σ_{ac}) with the frequency for different SBS/PAni.DBSA blends: (a) SPAni$_{EM}$, (b) SPAni$_R$, and (c) SPAni$_{IN}$ systems.

The variation of ac conductivity with applied frequency for all composition is illustrated in Figure 4, in which it is possible to observe a strong frequency dependence of this property especially at higher frequency. However, at lower end of frequency, the slope of conductivity frequency plot reduces significantly, which indicates more and more contribution of dc conductivity in ac conductivity which also testifies that there may be electrode polarization especially at low frequency region that might have some contribution in the increase in dielectric constant as the frequency is lowered. Therefore, the presence of interfacial polarization can be detected for some SBS/PAni.DBSA blends especially at lower concentration of PAni.DBSA. However, this contribution seemed to be relatively small as the matrix polymer is highly insulating in nature lowering the tendency of electrode discharge. It is also interesting to note that even at the lowest frequency region, the conductivity has some frequency dependency, which implies major contribution of MWS polarization in increment of dielectric constant.

Cole–Cole plots

In a system like SBS/PAni.DBSA blends in which there is a strong effect of conductivity especially at lower frequency region, the presence of any relaxation can be understood from a Cole–Cole plot. However, for present systems under investigation, the variations of loss factor and dielectric constant against frequency are very wide, spreading over several decades of magnitude. In these cases, it is recommended to express the Cole–Cole plot as a dependence of the log ε'' versus log ε' as illustrated in Figure 5.
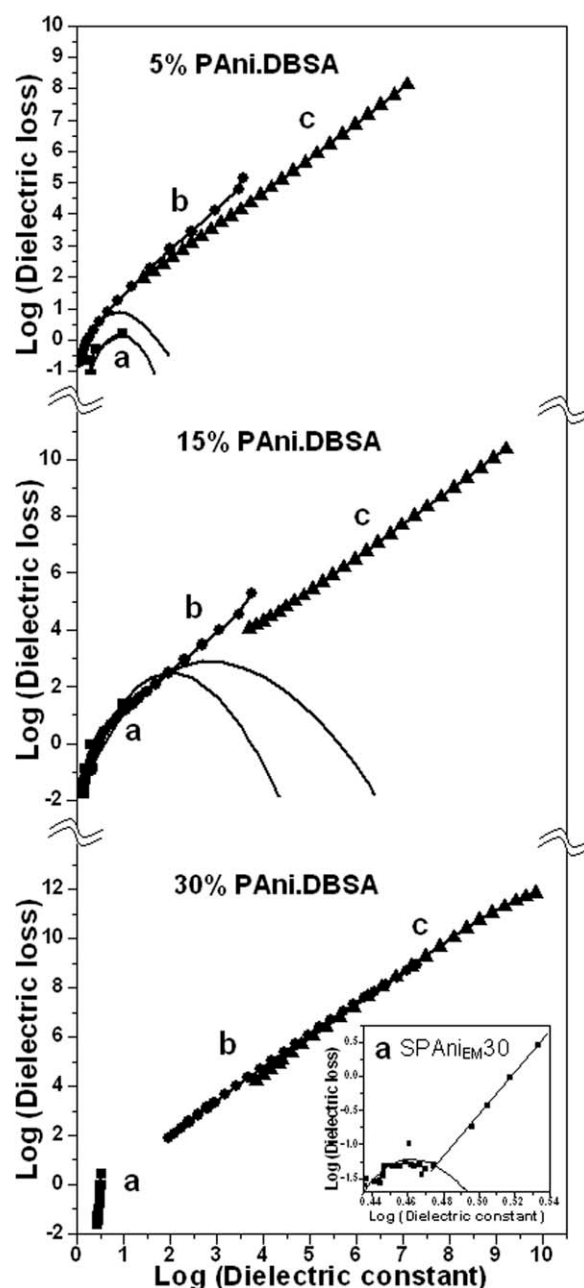

Figure 5 Modified Cole–Cole plot for different SBS-PAni blends: (a) SPAni$_{EM}$, (b) SPAni$_R$, and (c) SPAni$_{IN}$ systems.
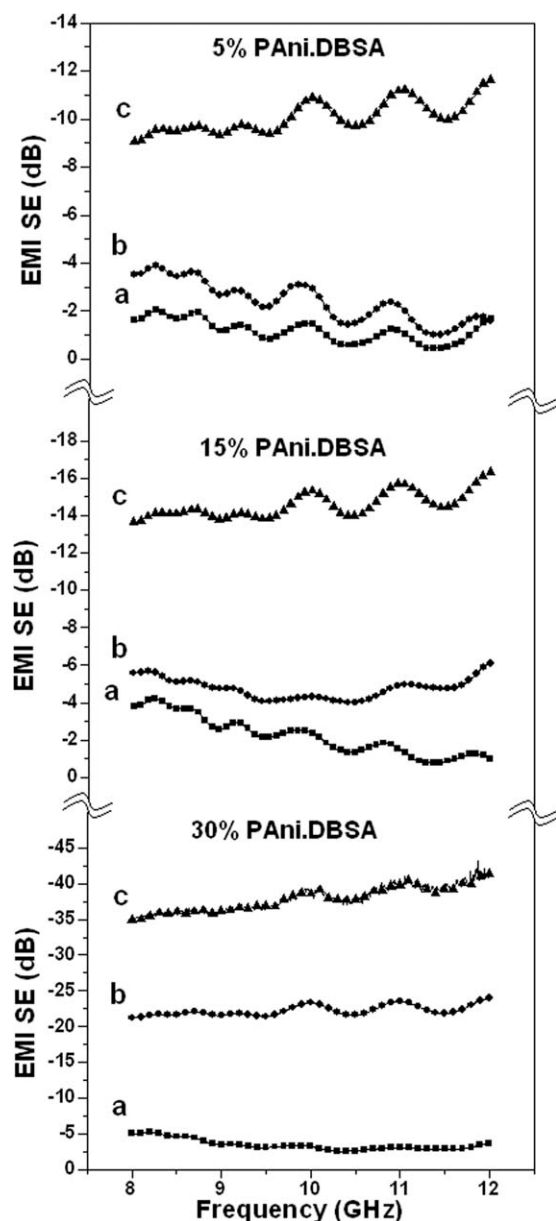
Figure 6 EMI SE of different SBS/PAni.DBSA blends in the X-band microwave frequency range of 7.8–12.4 GHz: (a) SPAni$_{EM}$, (b) SPAni$_R$, and (c) SPAni$_{IN}$ systems.

The SPAni$_{EM}$05 and SPAni$_R$05 systems presented some semicircular arcs at lower frequency region. SPAni$_R$05 also presented a straight line plot at higher frequency region like SPAni$_{IN}$05 systems, which presented only the linear plot. This circular arc is due to the interfacial polarization, and the linear increment is due to predominant effect of conductivity. Similar trend was observed for SPAni$_{EM}$15 and SPAni$_R$15 but not for SPAni$_{IN}$15, in which the plot was again linear. This signifies that the conductivity is a dominant factor for all SPAni$_{IN}$ blends. When the concentration of PAni.DBSA was increased to 30 wt %, the circular arc part was vanished for all SBS/PAni.DBSA systems and linear

plots are only observed, reflecting that composite systems become highly conducting with higher concentration (30 wt %) of PAni. For SPAni$_{EM}$30, the Cole–Cole plot seemed to be linear and vertical and somewhat different from the other two blends. This is because the change of log ε'' against log ε' for this system is much lower than in the other two systems. However, when the modified Cole–Cole plot for this blend is built separately (inset picture), the circular arc can also be detected.

EMI shielding effectiveness

The overall EMI SE in the X-band of SBS/PAni.DBSA blends is illustrated in Figure 6, as a function of the blend preparation, PAni.DBSA preparation, and concentration. For all set of blends, the increase in PAni.DBSA content resulted in an improvement of EMI SE. However, this property is strongly dependent on the method used for the preparation of PAni.DBSA (emulsion or redoped process) as well as the blend preparation (*in situ* polymerization versus physical blend). In fact, SPAni$_{IN}$ blends (produced by the *in situ* polymerization) presented substantially higher EMI SE when compared with both types of physically mixed blends (SPAni$_R$ and SPAni$_{EM}$ series) containing similar amount of PAni.DBSA. SPAni$_{IN}$ blend containing 30 wt % of PAni.DBSA presented an EMI SE between −35 to −40 dB in all frequency range studied. Generally, EMI SE of conductive composite systems is found to depend on its conductivity as discussed in the EMI SE theory.[12,42,43] SPAni$_{IN}$ series exhibited the highest EMI SE and also the highest conductivity when compared with those systems prepared by mechanical mixing. Regarding physical blends, those containing PAni.DBSA prepared by redoping process displayed higher EMI SE, which is in accordance with their respective conductivities. The EMI SE found in the SPAni$_{IN}$ blend series developed in this work is significantly higher (−35 to −40 dB with 30% of PAni.DBSA) than that presented in our previous work related to STF/PAni.DBSA with similar conductivity values (around −14 dB).[32] The better efficiency found in the current study for SBS/PAni.DBSA may be related not only to the conductivity values but also to the morphology characterized by the presence of microtubules of PAni.DBSA. Both matrices are constituted by styrene and butadiene block copolymer; however, the middle block in SBS is constituted by polybutadiene, and in the case of STF, the middle block is formed by styrene-*co*-butadiene copolymer. The composition of SBS imparts more flexibility to the polymer chain and facilitates the dispersion of PAni.DBSA and the formation of the microtubules.
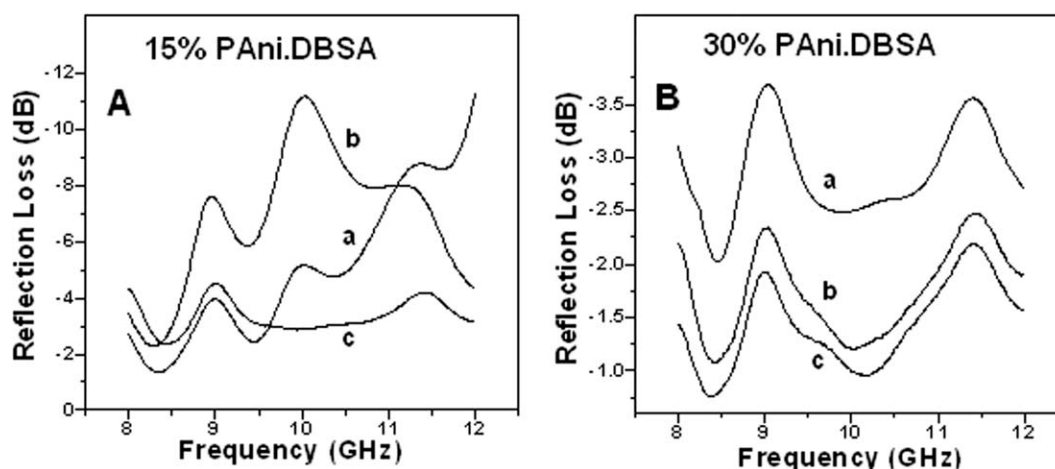
Figure 7 Reflection loss of different SBS/PAni.DBSA blends in the X-band microwave frequency range of 7.8–12.4 GHz: (a) $SPAni_{EM}$, (b) $SPAni_R$, and (c) $SPAni_{IN}$ systems.

Reflection loss

The total EMI SE consists of three components, namely, reflection (R), internal reflection (I), and absorption (A), as discussed earlier.[1,3,39] Metals generally show high EMI SE mainly because of reflection, whereas for lossy dielectrics, the absorption is considered the main contribution to the total EMI SE. The effect of the internal reflection is relatively much less in most of the cases. The dependence of the reflection loss with the frequency for SBS/PAni.DSA blends is illustrated in Figure 7, as a function of blend preparation, PAni.DBSA preparation, and concentration. This variation is found to be wavy in nature for different blends. It is interesting to observe that the reflection loss increased as the concentration of PAni.DBSA increased. Moreover, for the same concentration of PAni.DBSA, this property was significantly affected by the PAni.DBSA nature and blend preparation. For blends containing 15 wt % of PAni.DBSA, those corresponding to the $SPAni_{EM}15$ resulted in a decrease of the reflection loss at higher frequency. The $SPAni_R15$ presented the lowest reflection loss value with a dip in this property at a frequency of around 10 Gz, and $SPAni_{IN}15$ blend presented the highest value. For this blend, two maxima of reflection loss (more negative value) were observed: at around 9 and 11.5 GHz. Considering the blends containing 30 wt % of PAni.DBSA, all systems displayed two dips of reflection loss: at around 9 and 11.5 GHz. The highest reflection loss was also observed for the $SPAni_{IN}30$ blend. These results indicate that the higher conductive blends resulted in higher total EMI SE but also higher reflection loss. According to the definition of reflection loss,[44] which is the degree of mismatch between the incident and reflected power, these results suggest that the EMI SE of the high conducting $SPAni_{IN}$ blends is mainly due to the reflection. The reflection

effect is caused by the presence of mobile charge carriers that interacts with the incident electromagnetic field.[42]

Conductivity and EMI SE

Figure 8 presents the dependence of EMI SE at the reference frequency of 10 GHz against dc conductivity for the SBS/PAni.DBSA blends developed in this work. The dc conductivity of extrinsically conductive systems is due to the formation of conductive network that occurs at critical concentration (percolation limit) of conductive filler. Beyond this critical concentration, the conductivity change for such system is only marginal. From Figure 8, it can be observed that the EMI SE values did not change significantly with the conductivity until a certain critical value. Beyond this point, which may be related to the percolation threshold, the EMI SE increased
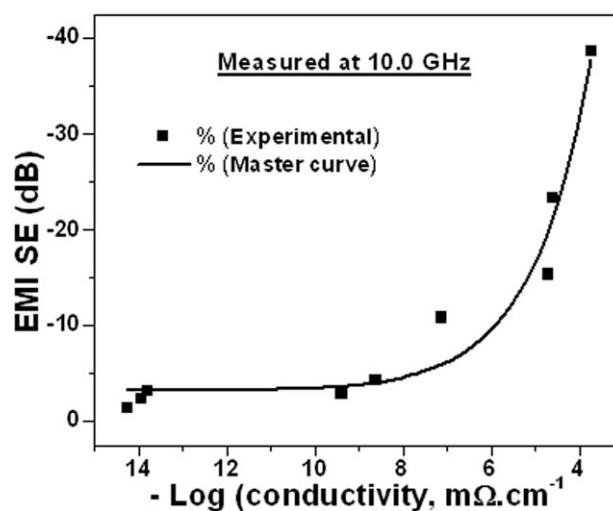

Figure 8 EMI SE versus dc conductivity of SBS/PAni.DBSA systems.

TABLE II
Different Parameters Value of the Fitted Curve Related to Eq. (9)

Parameter	Value	Error
Y_0	−3.17619	1.39755
A	−564.95632	364.40988
t	1.34059	0.29487

sharply, whereas the conductivity did not change significantly. This behavior was also found in other systems[45] and suggest that in addition to the conductivity, the continuous conductive network that is formed beyond the critical concentration of PAni.DBSA should be responsible for the high EMI SE. Beyond the percolation threshold, the conductive network becomes denser and interacts more efficiently with the incident electromagnetic radiation.[45]

From the results obtained for different SBS/PAni.DBSA blends, it was possible to build a unique master curve relating conductivity with EMI SE, using the following equation[45]:

$$Y = Y_0 + A \cdot e^{(-\sigma/t)}, \qquad (9)$$

where Y is the EMI SE at any point of conductivity σ, Y_0 is the initial value of EMI SE, and t is the decay constant. These parameters are given in Table II. The master curve, also presented in Figure 8, fits well with the experimental results and indicates that the EMI SE depends on the conductivity in exponential fashion but is not influenced by the method used for the blend preparation. Of course, the blends prepared by *in situ* polymerization are more conductive and contribute more for the sharp increase in EMI SE.

CONCLUSION

1. Resistivity, dielectrical properties, and EMI SE of different SBS/PAni.DBSA blends depend on the preparation method of PAni.DBSA, as well as its dispersion in SBS matrix. The presence of relaxation in different systems can be detected by modified Cole–Cole plots.
2. Considering physical blends, those prepared with redoped-PAni.DBSA (SPAni$_R$) exhibit lower resistivity, higher dielectrical properties, and EMI SE.
3. *In situ* polymerized SBS/PAni.DBSA blends show further improvement of electrical conductivity when compared with physical blends. These blends display higher dielectric constant and loss factor as well as higher EMI SE when compared with physically mixed SBS/PAni.DBSA blends.

4. A master curve is derived relating conductivity and EMI SE, which fits well with the experimental points.

The results obtained in this study confirm the effectiveness of *in situ* polymerization of aniline in the presence of SBS to produce PAni-based materials with better EMI SE characteristics.

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