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Study of Microwave Absorbing Properties of Polyaniline/STF Conducting Composites Prepared by *in Situ* Polymerization

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Summary: Conducting composites of polyaniline doped with dodecylbenzenesulfonic acid (PAni-DBSA) and poly(styrene-b-styrene-butadiene-b-styrene) (STF) as supporting matrix were prepared by *in situ* synthesis. The influence of composition and thickness on the electromagnetic properties and shielding effectiveness (SE) of the materials was evaluated using a microwave network analyzer and a standard rectangular waveguide from 8.2–12.4 GHz (X–band). It was found that the composition 49/51 exhibited the best SE and the higher values of reflected power (P_R), ε', ε'' and ε^*. The compositions 12/88 and 17/83 presented the higher values of transmitted power (P_T) and absorbed power (P_A), respectively. The composition 25/75 presented the higher value of tan δ. The thickness of 5$\times$ showed the best SE and higher value of P_R. The higher value of transmitted power (P_T) was obtained for thickness of 1$\times$. The values of P_A were similar for all thicknesses. The thickness of 1x showed the higher values of ε', ε'', ε^* and tan δ.

Keywords: *in situ* polymerization; microwave; polyaniline; shielding effectiveness

Introduction

Because of the increasing of electromagnetic pollution and the use of a great variety of commercial, military and scientific electro-electronic devices and systems, the interest in electromagnetic interference (EMI) shielding is receiving wide attention. The frequencies where the biggest interference problems occur are located in the ranges of 50–60 Hz (stereo system) and of 1–100 GHz.[1–6]

Diverse materials have been applied for EMI shielding, like typical metals as copper or aluminum, due to its high conductivity and dielectric constants, which contribute for high shielding effectiveness (SE). Despite the good mechanical and shielding properties, metals are heavy, are subject to corrosion, are difficult to process and to control SE.[3–6]

The conducting composites, especially those based on conducting polymers, have generated great interest due to the light weights, resistance to corrosion, good processing and easy conductivity control. Composites have been applied for absorption of electromagnetic radiation, due to possibility of variation of its conductivity with the radiation frequency of the incident waves, constituting the state of the art in the processing of Radiation-Absorbing Materials (RAM).[3,7–9]

The conducting polymers have been studied as additive in the processing of materials used in electromagnetic interference and microwaves absorption, in substitution to conventional absorbing materials, as ferrites and metallic and carbon particles. The interest in their application is due to easiness of preparation and attainment of RAM with lower specific mass. The use of RAM has increased

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Figure 1.
Network analyzer (a) and rectangular waveguide (b).

Table 1.
Ani and STF mass (g), ratio Ani/STF (% w/w), PAni-DBSA/STF experimental mass (g), PAni-DBSA/STF compositions (% w/w) and volume resistivity (R_V).

Ani mass (g)	STF Mass [a] (g)	Ratio Ani/STF before synthesis (% w/w)	PAni-DBSA/STF experimental mass [b] (g)	Ratio PAni-DBSA/STF after synthesis [c] (% w/w)	R_V (Ω.cm)
7.0	–	100/0	–	–	0.24E00
7.0	7.0	50/50	13.7	49/51	2.07E04
7.0	10.5	40/60	16.1	35/65	3.38E04
7.0	16.3	30/70	21.7	25/75	2.72E04
7.0	28.0	20/80	33.8	17/83	2.14E05
7.0	63.0	10/90	71.7	12/88	2.14E07
—	7.0	0/100	–	–	3.10E12

[c]Ratio = [(b − a)/(b)].100%

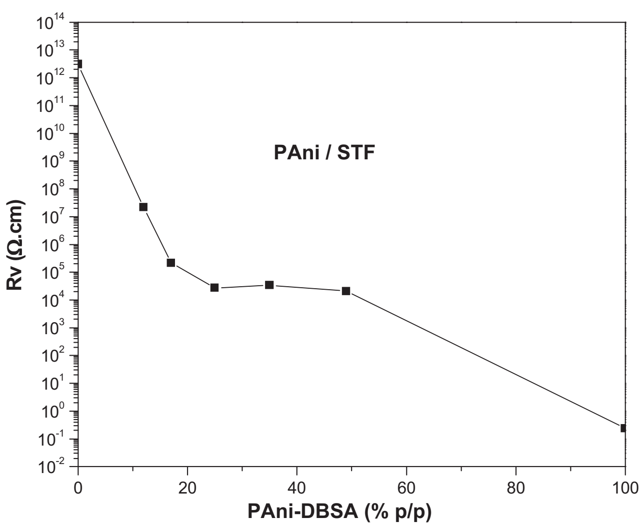

Figure 2.
Volume resistivity (Rv) of PAni-DBSA/STF composites.

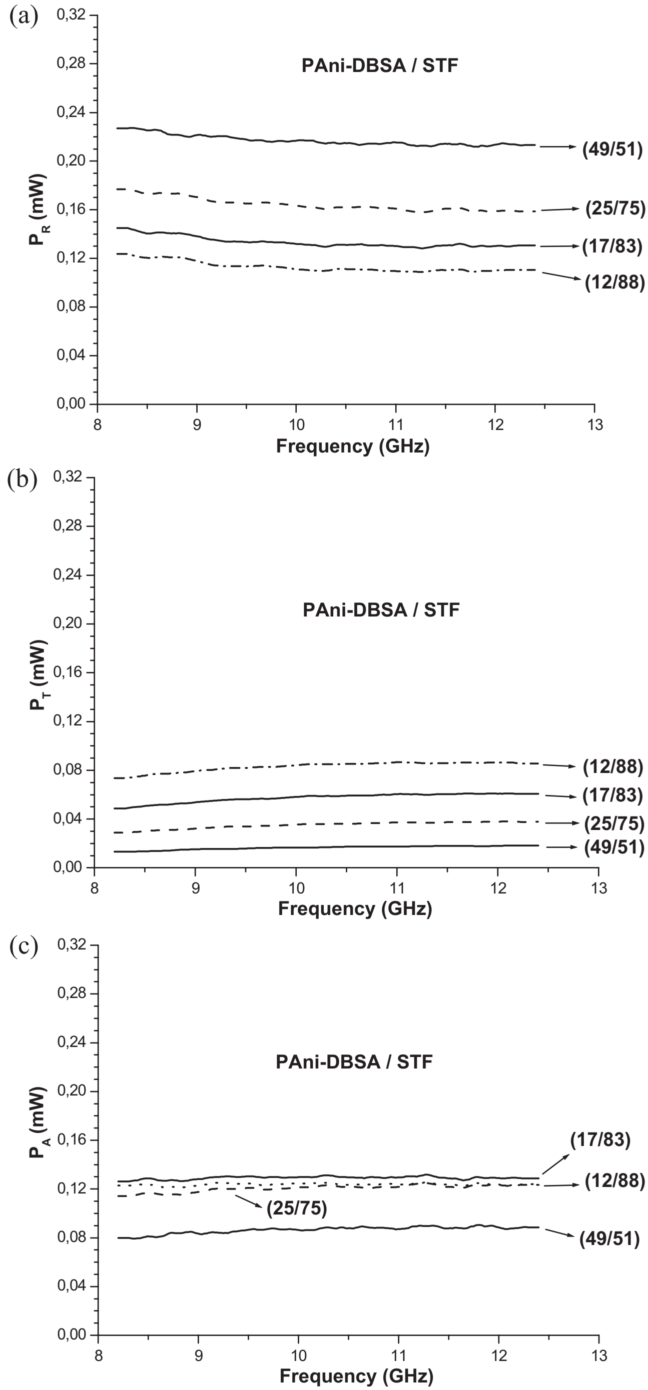

Figure 3.

Influence of composition on (a) Reflected Power (P_R), (b) Transmitted Power (P_T) and (c) Absorbed Power (P_A) (*vs.* Frequency) of PAni-DBSA/STF composites.

significantly, being applied in television sets, computers, cellular telephones, transmission and reception antennas, and communication and security systems used in automotives, ships and aircraft.[3]

RAM can be produced through deposition or mixture of conducting material on a matrix. Conducting polymers are of interest because of the good stability in ambient conditions, when used in polymeric blends.[3,9]

Polyaniline (PAni) has received a great attention in recent years, being extensively studied due to its molecular structures, easiness of polymerization and doping, excellent physical chemical properties (as chemical stability of its conducting form), low cost and easiness of attainment of its monomer, characteristics that make it a very efficient RAM.[7,8,11–13] Blends of polyaniline with thermoplastics constitute a very useful approach for the development of conducting materials with good processability and good mechanical properties.[14,15]

In this study, we report the preparation by *in situ* polymerization of conducting composites based on polyaniline doped with DBSA and poly(styrene-b-styrene-butadiene-b-styrene) (STF) as supporting matrix. The influence of composition and thickness of the materials on the electromagnetic properties and shielding effectiveness was evaluated using a microwave network analyzer and a standard rectangular waveguide from 8.2–12.4 GHz (X–band).

Experimental Part

Materials

Aniline (Ani) from Merck (Brazil) was distilled under reduced pressure before use. Ammonium peroxydisulfate (APS) (analytical grade from Vetec, Brazil), dodecylbenzene sulfonic acid (DBSA) (analytical grade from Fluka), toluene and methanol (analytical grades from Vetec, Brazil), and STF [poly(styrene-b-styrene-butadiene-b-styrene), 2G66, styrene content = 65%, density = 0.99 g.cm^{-3} from Basf, Brazil] were used without further purification.

Synthesis of Polyaniline Doped (PAni-DBSA) and PAni/STF Composites

PAni-DBSA was synthesized by one step route using toluene as the solvent. In a typical procedure 3.265 g (0.01 mol) of DBSA were dissolved in 100 ml of the solvent. 0.933 g (0.01 mol) of aniline was

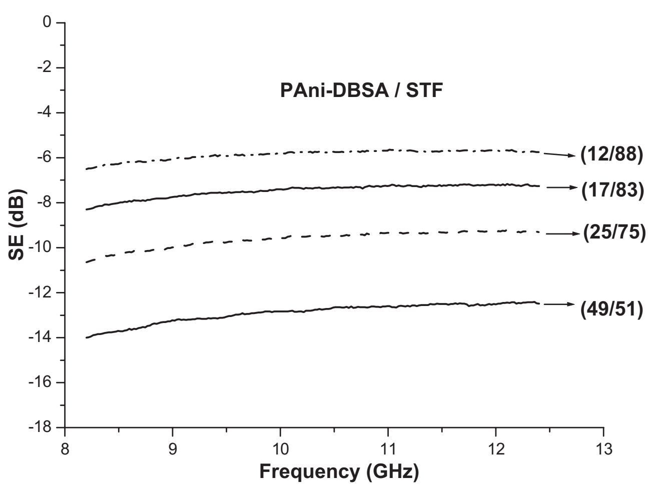

Figure 4.
Influence of composition on SE (*vs.* Frequency) of PAni-DBSA/STF composites.

added and the solution was cooled until 0–5 °C with constant stirring (350 rpm) for 30 min. Then, an aqueous solution of 2.28 g (0.01 mol) of APS was slowly added (drop by drop).

PAni-DBSA/STF composites were prepared by *in situ* polymerization of aniline in a toluene solution of STF at different ratio Ani/STF (% w/w). 24.4875 g (0.075 mol) of DBSA and different amounts of STF were dissolved into 250 ml of toluene. The medium was cooled at 0–5 °C and 7.0 g (0.075 mol) of aniline was added under stirring. After 30 minutes, an aqueous solution of 17.1135 g (0.075 mol) of APS was slowly added.

Both syntheses were performed at 0–5 °C for 6 h. The products were precipitated into methanol, filtered, washed several times with methanol and dried under reduced pressure for 24 h.

Volume Resistivity

The volume resistivity (R_V) measurements were performed using a Keithley 6517A electrometer and a two-plaques technique (ASTM D-257) to PAni-DBSA/STF composites, and conventional four-probe method to PAni-DBSA.[16,17] The composites and STF samples were molded by pressing for 2 min at 120 °C and 7.5 tonf. The PAni-DBSA sample was molded by

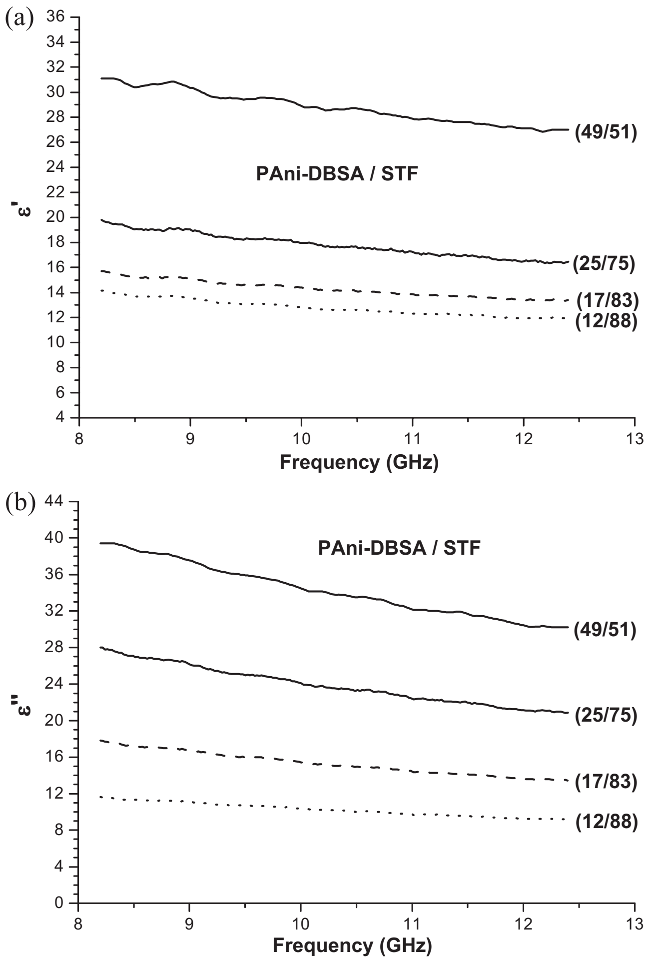

Figure 5.
Influence of composition on ε′ (a) and ε″ (b) (*vs.* Frequency) of PAni-DBSA/STF composites.

pressing the dried and milled powder at room temperature and pressure of 80 kgf.cm^{-2} for 5 min.

Electromagnetic Properties

The electromagnetic properties of PAni-DBSA/STF composites were measured from 8.2 to 12.4 GHz (X–band) using a microwave vector network analyzer Agilent PNA-L N5230C (Figure 1a) and a standard rectangular waveguide (Figure 1b). A two-port calibration was performed before testing in order to reduce or remove errors.[18,19] Agilent 85071 software was used to determine the real (ε', μ') and imaginary (ε'', μ'') parts of complex dielectric permittivity (ε^*) and complex magnetic permeability (μ^*), and the loss tangent. The shielding effectiveness (SE), reflected power (P_R), transmitted power (P_T) and absorbed power (P_A) were calculated from complex scattering parameters that correspond to reflection (S^*_{11}) and transmission (S^*_{21}). The composites samples were molded by pressing for 2 min at 120 ^{O}C and 7.5 tonf.

Results and Discussion

Table 1 shows Ani and STF mass (g), ratio Ani/STF (% w/w) used for this study, PAni-

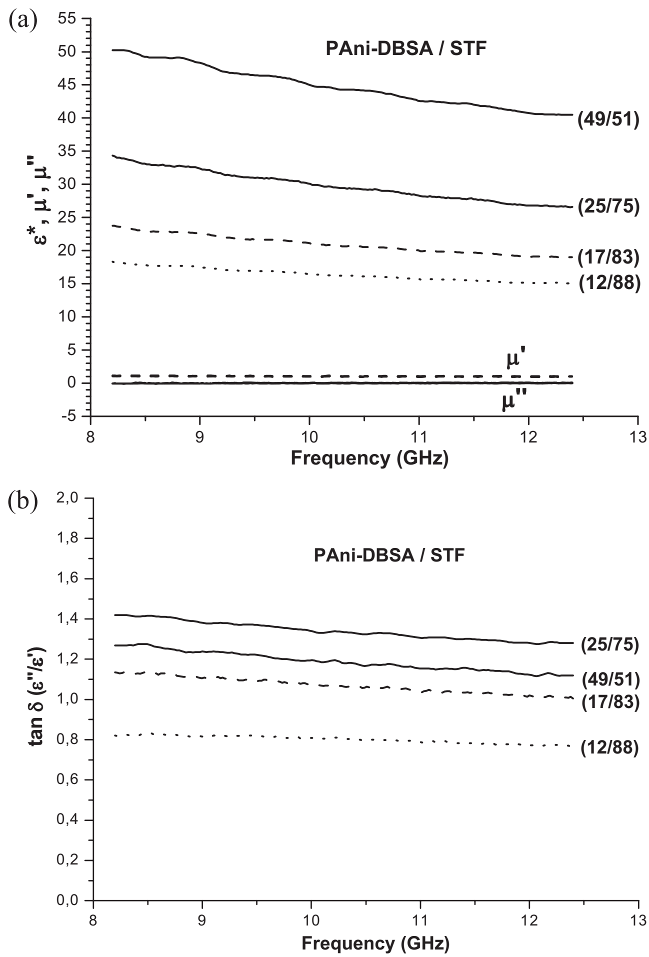

Figure 6.
Influence of composition on ε^*, μ', μ'' (a) and tan δ (b) (*vs.* Frequency) of PAni-DBSA/STF composites.

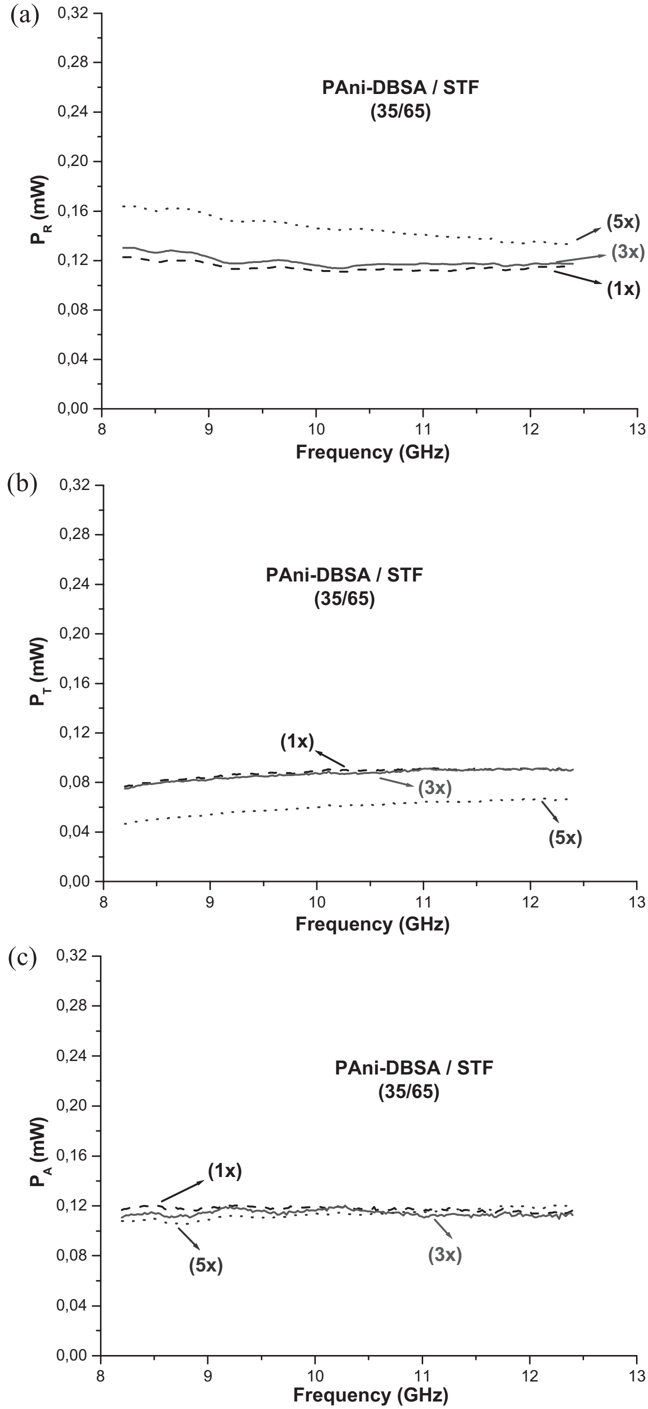

Figure 7.
Influence of thickness on (a) Reflected Power (P_R), (b) Transmitted Power (P_T) and (c) Absorbed Power (P_A) (*vs.* Frequency) of PAni-DBSA/STF composites.

DBSA/STF experimental mass (g) and PAni-DBSA/STF compositions (% w/w) after syntheses. Table 1 and Figure 2 show volume resistivity values of all materials.

As expected, volume resistivity values decrease with the increasing concentration of the conducting component. A small percentage (% w/w) of doped polyaniline (12%) produces a significant reduction in the volume resistivity (5 orders of magnitude), when compared to the volume resistivity of the pure supporting matrix. Compositions containing polyaniline concentration higher than 20% exhibited similar resistivity values, with a gain of 8 orders of magnitude.

Effect of Composition

The influence of composition on reflected, transmitted and absorbed power (Figure 3), shielding effectiveness (Figure 4), dielectric permittivity (ε', ε'', ε^*) (Figures 5 and 6a) and loss tangent (Figure 6b) of PAni-DBSA/STF composites was measured from 8.2 to 12.4 GHz (X–band) with a rectangular waveguide for all compositions. Sample 35/65 was used for analysis of the effect of the composite thickness on the obtained results. The real and imaginary parts of complex magnetic permeability (μ' e μ'') are shown in Figure 6a. The power values and shielding effectiveness were calculated with the Equations 1–4:[18,19]

$$P_R = P_I(S*_{11})^2 \quad (1)$$

$$P_T = P_I(S*_{21})^2 \quad (2)$$

$$P_A = P_I - (P_R + P_T) \quad (3)$$

$$SE = 20 \log S*_{21} \quad (4)$$

where P_I is the power of incident microwave (-5 dBm $= 0.32$ mW).

Composition 49/51 exhibited 96% of shielding effectiveness (-14 dB at 8.20 GHz) and the higher values of P_R (0.227 mW at 8.35 GHz), corresponding to 70,94% of incident power, dielectric constant (ε'), dielectric loss (ε'') and ε^*. For all systems P_R, SE, ε', ε'', ε^* and tan δ increase with addition of PAni-DBSA in the composites and gradually decrease with increase in frequency. Compositions 12/88 e 17/83 showed the higher values of P_T (0.067 mW at 12.13 GHz) and P_A (0.133 mW at 10.28 GHz), corresponding to 20.9% and 41.6% of incident power, respectively. Composition 25/75 presented the higher value of tan δ. The value of ε' is related to material capacity to store energy and ε'' expresses the material ability to dissipate energy. The loss tangent represents the speed of electromagnetic energy dissipa-

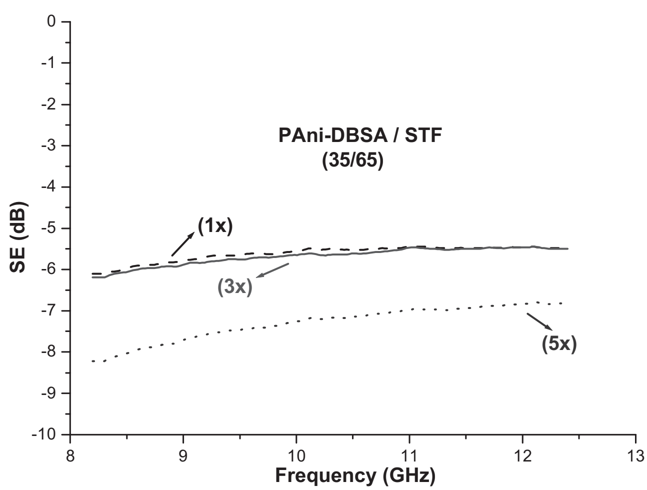

Figure 8.
Influence of thickness on SE (*vs.* Frequency) of PAni-DBSA/STF composites.

tion.[3] The values of real and imaginary parts of complex magnetic permeability ($\mu' = 1$ e $\mu'' = 0$), in the whole frequency range, indicate that all obtained composites are non-magnetic materials.[18,19]

Shielding effectiveness and the conductivity are related in the form:

$$SE = 20\log(1 + \sigma d Z_0/2),$$

where σ is the conductivity $(\text{ohm.cm})^{-1}$, d is the thickness of the sample, and Z_0 is the free-space wave impedance (377 ohm).

This form demonstrates that SE is proportional to the conductivity of the material. According to Mohanraj *et al.* [20] the increase in the contents of conductive filler increases the conductivity of the composite and consequently the SE. The conducting mesh formed by the conductive filler in the insulating matrix absorbs the electromagnetic waves. Increasing the filler contents increases the mesh and the interaction with the electromagnetic waves. So absorption increases and hence the SE.

Effect of Thickness

The influence of thickness on reflected, transmitted and absorbed power (Figure 7), shielding effectiveness (Figure 8), dielectric permittivity (ε', ε'', ε^*) (Figures 9–10a) and

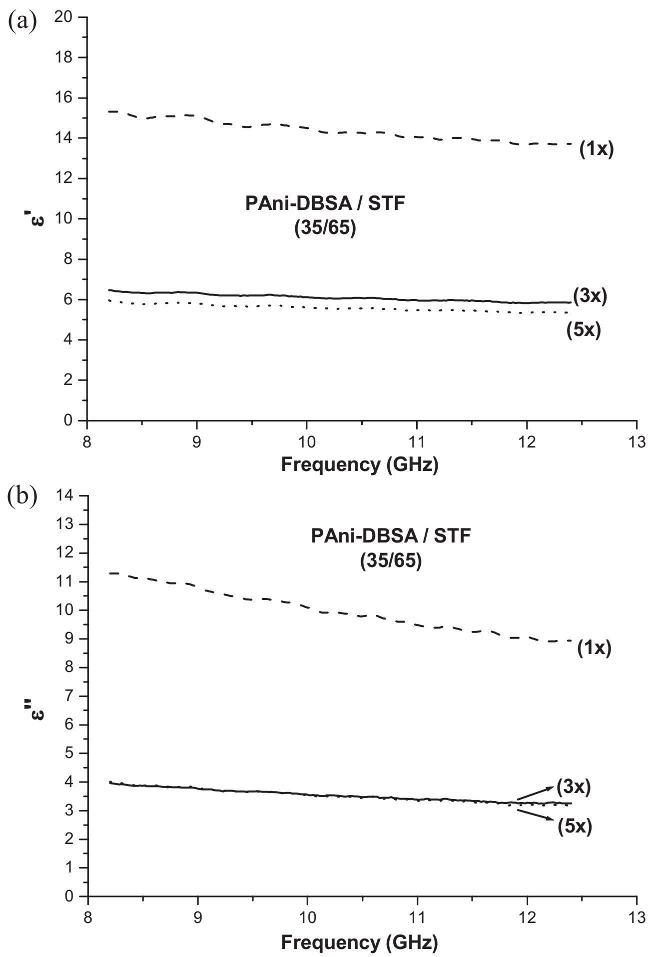

Figure 9.
Influence of thickness on ε' (a) and ε'' (b) (*vs.* Frequency) of PAni-DBSA/STF composites.

loss tangent (Figure 10b) was evaluated for three different thicknesses (named of 1×, 3× and 5×) of PAni-DBSA/STF 35/65.

Thickness of 5× showed 85% of shielding effectiveness (−8.2 dB a 8.2 GHz) and higher value of P_R (0.164 mW at 8.20 GHz), corresponding to 51.25% of incident power. The higher value of transmitted power (P_T) was obtained for thickness of 1× (0.092 mW at 11.06 GHz), corresponding to 28.8% of incident power. The P_A values were similar for all thicknesses. The values of P_R, SE, ε', ε'', ε^* and tan δ decrease with increase in frequency. It can be observed that SE increases continuously with increasing in thickness. The increasing in sample thickness produces higher amount of conducting mesh and interception of individual conducting layers, which affects both absorption and internal reflection, thus contributing to the increase in SE with thickness.[20] The thickness of 1x exhibited the higher values of ε', ε'', ε^* and tan δ, which is according to Jadhav and Puri[21] that showed ε' depends on thickness. For higher thickness ε' is lower in X band. The dielectric loss and tan δ show similar behavior to dielectric constant. The values of real and imaginary parts of complex magnetic permeability (Figure 14), for all thicknesses, indicate that composition 35/65 is a non-magnetic material.

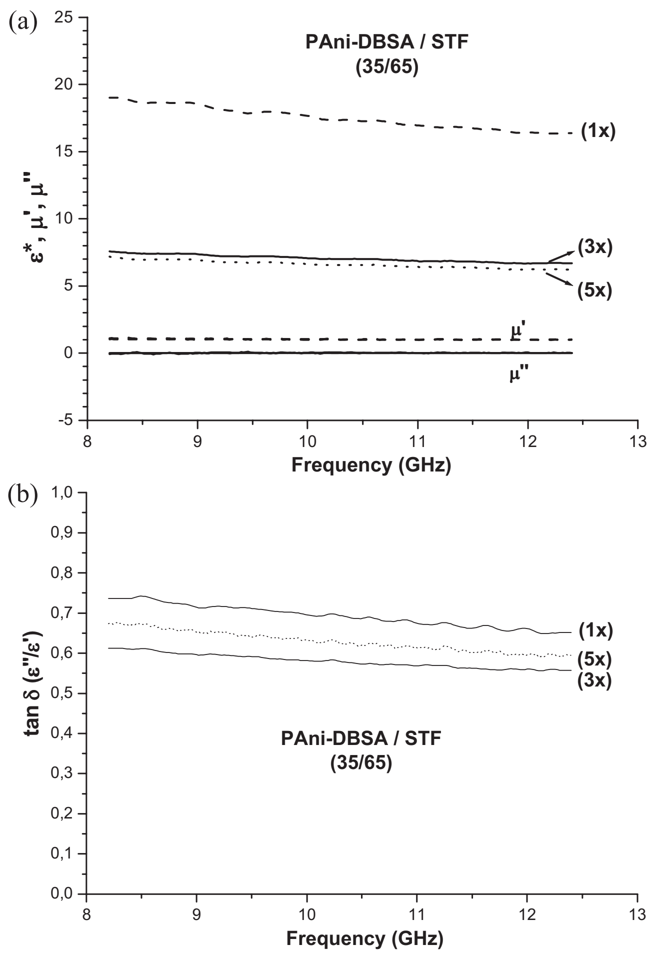

Figure 10.
Influence of thickness on ε^*, μ', μ'' (a) and tan δ (b) (*vs.* Frequency) of PAni-DBSA/STF composites.

Conclusion

The study of the influence of composition and thickness on electromagnetic properties and shielding effectiveness of PAni/STF conducting composites prepared by *in situ* polymerization, measured from 8.2 to 12.4 GHz (X–band) using a microwave vector network analyzer and a standard rectangular waveguide, showed that the best SE and the higher values of reflected power, dielectric constant, dielectric permittivity and dielectric loss were obtained when the contents of the conducting composite were larger. The higher value of loss tangent was observed at composition 25/75. There was no influence of thickness on the absorbed power. The best SE value was obtained with the larger thickness. The higher values of dielectric constant, dielectric loss, dielectric permittivity and loss tangent were obtained with the smallest thickness.

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