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RESEARCH ARTICLE



Electromagnetic interference shielding effectiveness and microwave absorption properties of thermoplastic polyurethane/montmorillonite-polypyrrole nanocomposites

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KEYWORDS

montmorillonite, polypyrrole, shielding effectiveness, thermoplastic polyurethane

1 | INTRODUCTION

Electromagnetic interference (EMI) has become a technical problem in the modern world because of the rapid proliferation of electronic and telecommunication systems, which emit electromagnetic radiation and may perturb the performance of electronic devices. To prevent EMI and increase the device efficiency and lifetime, many studies have been focused in producing electromagnetic radiation shielding or absorbing materials. In this context, electrically conducting polymer composites composed of intrinsically conducting polymer (ICP), such as polypyrrole (PPy) and polyaniline (PAni), dispersed in an insulating polymer matrix have attracted much interest for EMI shielding applications.¹⁻¹² The scientific and technological interest for producing these materials is due to their lightweight, corrosion resistance, design flexibility, good processability, physical properties of polymeric materials, high electromagnetic interference shielding effectiveness (EMI SE), and good microwave absorption properties.^{3,13-22} For many applications, the EMI SE value of 15 to 30 dB is considered satisfactory and corresponds to 99.9% attenuation of the EMI radiation.^{13,23} Electromagnetic interference shielding effectiveness is influenced by 3 mechanisms: reflection (SE_R), absorption (SE_A), and multiple reflections (SE_M) of the electromagnetic waves. The attenuation of EMI by absorption has been preferred instead of reflection because of the increase demand of microwave absorbing materials.^{24,25} Usually, microwave absorbing materials must display an electrical conductivity in the range of 10⁻⁴ and 10⁻¹ S/cm.⁴

A major challenge in developing shielding composites based on PPy or PAni is how to disperse the ICP particles into insulating polymer matrix to achieve the highest EMI SE and electrical conductivity values at lower ICP content. According to the literature, many studies have demonstrated that the incorporation of nanostructured conductive additives based on montmorillonite-ICP (Mt-ICP) into insulating polymer matrix induces higher electrical conductivity and EMI SE values WILEY-advanced -

when compared with those values found for conducting blends composed of neat PPy or PAni dispersed into the same polymer matrix.^{3,7,8,10,15,26} This behavior is assigned to the higher aspect ratio of Mt-ICP and better dispersion of these conducting nanoparticles than those found for ICP particles. Moučka et al³ have compared the electrical properties of polypropylene (PP)/Mt-PPy nanocomposites with those PP/PPy blends. The PP/Mt-PPy composites have presented SE_A value 3 times higher than that of PP/PPy blends. According to Moučka et al,³ this behavior is related to the high dielectric loss factor of PP/Mt-PPy composites because of the polarization effect produced by the anisotropic Mt-PPy nanoparticles. In our previous study, we have reported the production of a novel flexible and highly conducting nanocomposites based on Mt-PPy-filled thermoplastic polyurethane (TPU).²⁷ The TPU/Mt-PPy nanocomposites showed electrical conductivity as high as 0.05 S/cm and lower percolation threshold (approximately 10 wt%) than those found for TPU/PPy blends. However, the effect of the Mt-PPy content on the EMI SE values and microwave absorption properties of TPU/Mt-PPy has not been explored. In this study, the microwave absorption properties of TPU/ Mt-PPy nanocomposites and their potential use for EMI applications were investigated. In addition, to the best of our knowledge, no works mention the characterization of TPU/Mt-PPy nanocomposites for EMI applications.

2 | EXPERIMENTAL

2.1 | Materials

Pyrrole monomer, 98%, purchased from Sigma-Aldrich (Germany) was distilled under vacuum and stored in a refrigerator before use. Iron (III) chloride hexahydrate, FeCl₃.6H₂O, analytical grade (Vetec, Rio de Janeiro, Brazil), and dodecylbenzenesulfonic acid (DBSA, Sigma-Aldrich, Italy) were used as received. Sodium bentonite clay (Mt), VULGEL CN 45, is a product of Aliança Latina Indústrias e Comércio Ltda (Uruguaiana, Rio Grande do Sul, Brazil) and was offered by loto International–Divisão de Masterbatches (Campo Magro, Paraná, Brazil). Commercially available TPU (Elastollan 1180 A10 extrusion grade; Shore A hardness = 80, density = 1.11 g/cm) based on polyether was purchased from Basf (São Paulo, Brazil).

2.2 | Synthesis of conducting fillers

The preparation of conducting fillers, such as montmorillonitedodecylbenzenesulfonic acid-doped polypyrrole (Mt-PPy.DBSA), montmorillonite-hydrochloride acid-doped polypyrrole (Mt-PPy.Cl), dodecylbenzenesulfonic acid-doped polypyrrole (PPy.DBSA), and hydrochloride acid-doped polypyrrole (PPy.Cl), was described in our previous study.²⁷

2.3 | Production of TPU mixtures

Thermoplastic polyurethane mixtures were prepared as described in our previous study.²⁷ The TPU matrix with different conductive filler content was melt blended using a Haake Polylab QC (internal mixer) at 170°C during 15 minutes and with a rotor speed of 50 rpm. Then,

composites were compressed at 170°C for 5 minutes less than 12 MPa pressure and cooled to room temperature to form plates and disks. Before processing, TPU and conductive fillers were dried in a circulating air oven at 100°C for 3 hours and vacuum oven at 60°C for 12 hours, respectively.

2.4 | Characterization techniques

2.4.1 | Electrical conductivity

Direct current electrical conductivity (σ_{DC}) measurements for neat TPU and high-resistivity TPU nanocomposites (<10⁻⁷ S/cm) were performed using the 2-probe standard method with a Keithley 6517A electrometer connected to Keithley 8009 test fixture, at room temperature.

The electrical conductivity of conductive fillers and low-resistivity TPU nanocomposites ($\sigma_{\rm DC} > 10^{-7}$ S/cm) was measured at room temperature using the 4-probe standard method with a current source (Keithley 6220) and an electrometer (Keithley model 6517A).²⁸

2.4.2 | Electromagnetic interference shielding efficiency and dielectric properties

The EMI SE and dielectric properties of TPU nanocomposites were measured using a standard rectangular waveguide and a 2-port vector network analyzer (model PNA-L N5230C, Agilent Technologies, Santa Clara, California) in the frequency range from 8.2 to 12.4 GHz (X-band). The real (dielectric constant, ε') and the imaginary parts (dielectric loss, ε'') of the permittivity of the different composites were determined by Agilent 85071 software.

The EMI SE can be measured and quantified by the amount of electromagnetic radiation attenuated in a specific material. In this work, EMI SE was calculated based on the S_{12} (S_{21}) measurements (S-parameters)^{29,30} according to Equation 1.

$$\mathsf{EMISE} \ (dB) = 10 \log_{10} \frac{1}{\left|\mathsf{S}_{12}\right|^2} + 10 \log_{10} \frac{1}{\left|\mathsf{S}_{21}\right|^2} \tag{1}$$

where $|S_{12}|$ represents the transmitted power from port 1 to port 2.

2.4.3 | Morphology

The microstructures of TPU nanocomposites were analyzed by using field emission scanning electron microscope (FESEM) and transmission electron microscopy. The FESEM observations were performed by using a JEOL FESEM model JSM-6701F (JEOL, Peabody, Massachusetts) at an accelerating voltage of 10 kV. The samples were fractured in liquid nitrogen and coated with gold.

Transmission electron micrographs were conducted by a Phillips CM120 microscope (Phillips, Germany) at an accelerating voltage of 80 kV. Samples consisting of 60-nm-thick ultrathin sections were obtained by a Leica Ultracut UCT ultramicrotome (Leica, Germany) equipped with a diamond knife and deposited on copper grids.

RAMOA ET AL

3 |

3.1 | Effect of conducting filler content and type on the EMI attenuation mechanism

RESULTS AND DISCUSSION

Total EMI SE is described as the sum of 3 EMI attenuation mechanisms: reflection loss (SE_R), absorption loss (SE_A), and multiple internal reflection loss at the material interface (SE_M) (conductive fillers or porosity). In this study, the multiple reflection effects were ignored because they cannot be measured as a separate factor.^{2,31} The transmittance (*T*) and reflectance (*R*) coefficients were obtained through the S-parameters determined from the vector network analyzer,^{9,31,32} according to Equations 2 and 3:

$$T = |E_T/E_I|^2 = |S_{12}|^2 \left(=|S_{21}|^2\right)$$
(2)

$$R = |E_R/E_I|^2 = |S_{11}|^2 \left(=|S_{22}|^2\right)$$
(3)

The absorbed coefficient was calculated considering that the incident power used in the experiments was 5 dB by Equation 4.

$$A = I - T - R \tag{4}$$

The total EMI average, absorption loss (SE_A), and reflection loss (SE_R) were calculated on the basis of transmittance (*T*) and reflectance (*R*) coefficients and calculated according to the following equations 9,31,32 5 to 7.

$$EMI SE = SE_R + SE_A = 10 \log I / I - R + 10 \log I - R / T = 10 \log I / T$$
 (5)

$$SE_{\rm R} = 10\log I/I-R \tag{6}$$

$$SE_{\rm A} = 10 \log I - R/T \tag{7}$$

The effect of conductive filler amount on the total EMI SE average, which includes the absorption and reflection phenomena, and electrical conductivity of nanocomposites is illustrated in Figure 1. The EMI SE measurements were performed at X-band frequency range (8.2 at 12.4 GHz) using samples thickness of 2 mm.

The total EMI SE average and electrical conductivity of all composites increased with increasing the filler content because of the formation of a conducting network into TPU matrix, as observed in the microstructures (Figure 2). Compared with TPU/PPy.Cl and TPU/PPy. DBSA blends, EMI SE and electrical conductivity of TPU/Mt-PPy.Cl and TPU/Mt-PPy.DBSA nanocomposites are higher. Moreover, the percolation threshold of TPU/Mt-PPy.DBSA (approximately 10 wt%) is lower than that of TPU/Mt-PPy.Cl (approximately 20 wt%) and TPU/PPy (>30 wt%) blends. As discussed in our previous study,²⁷ this behavior is attributed to the higher aspect ratio and better dispersion of Mt-PPy.DBSA filler into TPU matrix than those Mt-PPy.Cl and neat PPy particles.²⁷ In this study, it was also demonstrated that the nanostructured Mt-PPy.DBSA filler was partially exfoliated and/or intercalated in the TPU matrix, inducing a conducting network formation in the insulating polymer matrix at lower conductive filler content when compared with those intercalated Mt-PPy.Cl into TPU matrix. Moreover, above the percolation threshold, the SE_A becomes the main EMI shielding mechanism for both nanocomposites. This behavior is assigned to the conducting pathway formation into TPU matrix that facilitates the charge carrier movement and better electromagnetic



FIGURE 1 Effect of conductive filler content on the total electromagnetic interference shielding effectiveness (EMI SE) average, SE_A, SE_R, and electrical conductivity of blends and nanocomposites with a sample thickness of 2 mm [Colour figure can be viewed at wileyonlinelibrary.com]





FIGURE 2 Field emission scanning electron microscopic images of (A) TPU/PPy.CI, (B) TPU/Mt-PPy.CI, (C) TPU/PPy.DBSA, and (D) TPU/Mt-PPy. DBSA and transmission electron microscopic images of (E) TPU/PPy.DBSA and (F) TPU/Mt-PPy.DBSA. All mixtures were loading with 20 wt% of conductive filler

radiation interactions. Therefore, high electrical conductivity of EMI SE and SE_A for TPU/Mt-PPy nanocomposites can be observed with increasing conducting filler content, while SE_R value is remained practically the same. However, these effects were not observed for TPU/PPy.Cl or TPU/PPy.DBSA blends, probably because of the lower electrical conductivity values (lower than 10^{-10} S/cm), even for TPU/PPy blends filled with 30 wt% of PPy.

Table 1 summarizes the experimental values of the total EMI SE average, SE_A, SE_R, the EMI SE percentage by absorption, and skin depth. For TPU/PPy blends and TPU/Mt-PPy nanocomposites, SE_A increases, SE_R becomes constant, and skin depth is reduced with increasing filler content. This result highlights a relationship between skin depth, absorption mechanism, and filler content. The skin depth

(δ) (depth at which the field drops to 1/e of its original strength) is determined by (δ) = $\sqrt{1/\pi f \sigma \mu}$, where *f* is the frequency in Hz, σ is the conductivity in S/m, and μ is the magnetic permeability ($\mu = \mu_0 \mu_r$, where $\mu_0 = 4\pi \times 10^{-7}$ H/m and μ_r is the relative permeability).^{3,14,33,34} The SE_A for nanocomposites containing Mt-PPy.Cl and Mt-PPy.DBSA is higher than that found for TPU/PPy.Cl and TPU/PPy.DBSA blends, suggesting that the SE_A is influenced by the presence of Mt. Moučka et al³ have been reported similar results for PP/Mt-PPy composites. In that study, PP/Mt-PPy composites have shown SE_A value (60 dB) 3 times higher than that of PP/PPy blend (20 dB) at frequency of 1.5 GHz. According to those authors, this behavior can be related to the dielectric loss when compared with PPy blends.

VILEY-advanced 1381

TABLE 1 Total EMI SE average, SE_A, SE_R, percentage of EMI SE by absorption, and skin depth of blends and nanocomposites with sample thickness of 2 mm

Sample	Conductive Filler Content, wt%	Total EMI SE, dB	SE _A , dB	SE _R , dB	EMI SE by Absorption, %	Skin Depth, mm
TPU	0	1.2 ± 0.1	0.5 ± 0.0	0.8 ± 0.0	42	16.9 ± 2.7
TPU/PPy.Cl	10	3.6 ± 0.1	1.1 ± 0.1	2.5 ± 0.1	31	8.6 ± 1.2
TPU/PPy.Cl	20	5.7 ± 0.3	1.8 ± 0.1	4.0 ± 0.2	32	6.5 ± 0.8
TPU/PPy.Cl	30	7.1 ± 0.3	3.7 ± 0.1	3.4 ± 0.3	52	3.7 ± 0.4
TPU/Mt-PPy.Cl	10	4.8 ± 0.2	1.9 ± 0.1	2.9 ± 0.2	40	6.2 ± 0.8
TPU/Mt-PPy.Cl	20	9.0 ± 0.6	4.6 ± 0.2	4.3 ± 0.5	51	3.8 ± 0.7
TPU/Mt-PPy.Cl	30	10.9 ± 0.6	6.0 ± 0.9	4.0 ± 0.4	63	3.0 ± 0.2
TPU/PPy.DBSA	10	4.1 ± 0.1	1.5 ± 0.1	2.6 ± 0.1	36	7.1 ± 0.9
TPU/PPy.DBSA	20	6.5 ± 0.2	1.6 ± 0.1	4.9 ± 0.3	25	7.5 ± 1.0
TPU/PPy.DBSA	30	7.2 ± 0.2	2.5 ± 0.1	4.7 ± 0.3	35	5.9 ± 0.8
TPU/Mt-PPy.DBSA	10	8.4 ± 0.7	3.1 ± 0.2	5.3 ± 0.5	37	4.0 ± 0.4
TPU/Mt-PPy.DBSA	20	11.8 ± 0.6	7.8 ± 0.9	4.1 ± 1.3	66	2.8 ± 0.2
TPU/Mt-PPy.DBSA	30	16.6 ± 0.5	12.4 ± 0.9	4.2 ± 0.6	75	1.3 ± 0.2

Abbreviations: EMI SE, electromagnetic interference shielding effectiveness; Mt, montmorillonite; PPy.Cl, hydrochloride acid-doped polypyrrole; PPy.DBSA, dodecylbenzenesulfonic acid-doped polypyrrole; TPU, thermoplastic polyurethane.



FIGURE 3 Effect of the sample thickness (2 and 5 mm) on the total electromagnetic interference shielding effectiveness (EMI SE) average, SE_A, and SE_R of mixtures loading with 30 wt% of conductive filler

3.2 | Effect of sample thickness on the total EMI SE

Figure 3 shows the influence of sample thickness (2 and 5 mm) on the total EMI SE average of mixtures containing 30 wt% of conductive filler. As expected, EMI SE values of samples with thickness of 5 mm are higher than those with 2 mm thickness,6,35-37 except for TPU/ PPy blends. The result observed for TPU/PPy blends was probably related to the poor dispersion of neat PPy particles into TPU matrix, as shown in Figure 2A,C. The increase of EMI SE for TPU/Mt-PPy.Cl and TPU/Mt-PPy.DBSA nanocomposites can be assigned to the $\ensuremath{\mathsf{SE}_{\mathsf{A}}}$ mechanism, once the SE_R value was remained practically the same. Experimental values of total EMI SE, SE_A, SE_R, percentage of EMI SE by absorption, and skin depth for mixtures with 5 mm thickness are shown in Table 2. Thermoplastic polyurethane nanocomposite with 30 wt% of Mt-PPy.DBSA and 5 mm thickness showed EMI SE of approximately 36.5 dB, which is twice the value found for the same nanocomposite composition with 2 mm thickness (approximately 16.6 dB), and TPU/Mt-PPy.Cl samples with 5 mm thickness (approximately 17.5 dB).

TABLE 2 Total EMI SE average, SE_A, SE_R, percentage of EMI SE by absorption, and skin depth of blends and nanocomposites with sample thickness of 5 mm

Sample	Conductive Filler Content, wt%	Total EMI SE, dB	SE _A , dB	SE _R , dB	EMI SE by Absorption, %	Skin Depth, mm
TPU/PPy.Cl	30	5.3 ± 0.8	3.4 ± 0.4	1.9 ± 1.2	64	4.3 ± 1.2
TPU/Mt-PPy.Cl	20	12.4 ± 0.7	9.8 ± 0.5	2.6 ± 0.2	79	2.8 ± 0.3
TPU/Mt-PPy.Cl	30	17.5 ± 1.0	13.6 ± 1.5	3.9 ± 0.7	78	2.2 ± 0.4
TPU/PPy.DBSA	30	4.6 ± 1.2	3.2 ± 0.4	1.4 ± 0.9	70	12.0 ± 2.2
TPU/Mt-PPy.DBSA	20	20.4 ± 1.4	16.6 ± 1.8	3.8 ± 0.5	81	1.8 ± 0.3
TPU/Mt-PPy.DBSA	30	36.5 ± 2.8	32.0 ± 3.1	4.5 ± 0.4	88	1.2 ± 0.2

Abbreviations: EMI SE, electromagnetic interference shielding effectiveness; Mt, montmorillonite; PPy.CI, hydrochloride acid-doped polypyrrole; PPy.DBSA, dodecylbenzenesulfonic acid-doped polypyrrole; TPU, thermoplastic polyurethane.



FIGURE 4 Influence of the conductive filler content and frequency on the electromagnetic interference shielding effectiveness (EMI SE) value for thermoplastic polyurethane (TPU) and their mixtures



FIGURE 5 Dependence of real (ε') and imaginary (ε'') permittivity of blends and nanocomposites as a function of conducting filler content and frequency [Colour figure can be viewed at wileyonlinelibrary.com]

3.3 | Influence of X-band frequency range on the EMI SE

The dependence between EMI SE values and X-band frequency range for mixtures is illustrated in Figure 4. A slight decrease of EMI SE value is observed for all TPU/PPy blends and for composites containing Mt-PPy.Cl and Mt-PPy.DBSA below percolation threshold corresponding at 20 and 10 wt%, respectively. However, above the percolation threshold, both TPU/Mt-PPy.Cl and TPU/Mt-PPy.DBSA nanocomposites showed different behaviors because of the conducting network formation. For these materials, the EMI SE decreases approximately at 11 GHz and then increases for frequencies higher than 12 GHz. Gupta and Choudhary³³ have been explained the increase of EMI SE as a function of frequency due to the reduction of the material skin depth. The skin depth for nanocomposites is reduced with increasing the conductive filler and electrical conductivity. The TPU/Mt-PPy. DBSA nanocomposites presented the lowest skin depth and the highest EMI SE values, as observed in Tables 1 and 2.

3.4 | Dielectric properties of TPU composites

Figure 5 shows real (ε') and imaginary (ε'') permittivity of TPU and their mixtures with 2 mm sample thickness as a function of frequency. Both ε' and ε'' increase with increasing the conductive filler content because of the conducting pathway formation, which induces higher dipole concentration and interfacial polarization. As expected, ε' and ε'' of TPU/PPy blends are lower than those found for TPU/Mt-PPy nanocomposites because of the poor dispersion and distribution of neat PPy particles into TPU matrix, as shown in Figure 2. Better dispersion and distribution of Mt-PPy particles into TPU matrix promotes higher dipole concentration and interface polarization and, hence, increasing SE_A values. Moreover, above percolation threshold resonant effects (ε' and ε'') fluctuations with increasing frequency is observed for TPU/Mt-PPy nanocomposites. Furthermore, these effects are expected for composites containing conductive filler with high aspect ratio and high electrical conductivty.^{2,38}

4 | CONCLUSIONS

Flexible and highly conducting TPU/Mt-PPy nanocomposites were successfully obtained for using in electromagnetic shielding applications. The total EMI SE average and electrical conductivity values are influenced by the conducting filler type and concentration. The hybrid Mt-based fillers give rise to TPU conducting composites with better EMI SE than those prepared with pure PPy, highlighting the importance of the high aspect ratio of the former materials, which contributes for the formation of conducting pathway with lower amount of filler. Regarding the nanocomposites prepared with hybrid fillers, those involving Mt-PPy-DBSA presented the higher values of electrical conductivity and EMI SE. This behavior can be attributed to the better dispersion of Mt-PPy.DBSA filler within the TPU matrix, caused by the presence of the DBSA as the doping agent for the PPy component. The long alkyl group in this component acts as a compatibilizing agent between the filler and the matrix, contributing for a better dispersion. Electromagnetic interference attenuation mechanism was affected by

WILEY-advanced technologies 1383

the presence of Mt, once the absorption loss (SE_A) increases with increasing Mt-PPy.Cl or Mt-PPy.DBSA content into TPU matrix, contributing to enhance EMI SE values, which were significantly higher than those found for TPU/PPy blends. On the other hand, reflection loss (SE_R) is practically independent of Mt-PPy added into TPU matrix. Moreover, there is a relationship between skin depth, microwave absorption properties, and conducting filler type and content. The EMI SE values were also influenced by the sample thickness and frequency. The real (ϵ) and imaginary (ϵ) permittivity values for TPU/ Mt-PPy.DBSA nanocomposites were higher when compared with those observed for TPU/Mt-PPy.Cl nanocomposites and TPU/PPy blends. These results indicate that the highest absorption properties can be achieved for TPU/Mt-PPy.DBSA nanocomposites because of the good dispersion and distribution of Mt-PPy.DBSA conducting filler in the TPU matrix, inducing higher dipolar or/and interfacial polarization. On the basis of the results presented in this work, it can be concluded that the conductive nanocomposites composing of TPU/Mt-PPy.DBSA are promising materials for shielding/absorbing in the microwave region, especially X-band region.

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1384 WILEY-advanced

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