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Effect of PANI on Thermal, Mechanical and Electromagnetic Properties of HDPE/LLDPE/PANI Composites

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In this work, polyaniline (PANI) in emeraldine-base form, synthesized by chemical oxidation polymerization, was protonated with hydrochloric acid (HCl). Composites based on high-density polyethylene (HDPE) and linear-low density polyethylene (LLDPE) blends with PANI were prepared in molten condition using a torque rheometer. The effect of compatibilizer agent (maleic anhydride-grafted high density polyethylene, HDPE-g-MA) and different contents of PANI on the blends-based composites was also investigated. Thermal, mechanical, and electromagnetic (electric permittivity) measurements and morphological aspects of the composites were evaluated. The addition of PANI content in the composites decreases the degree of crystallinity of HDPE and LLDPE blends, which implies that PANI particles make it difficult for co-crystallization to occur in the HDPE and LLDPE, respectively. On the other hand, the addition of compatibilizer agent in the HDPE and LLDPE blends increased the degree of crystallinity. The complex parameters of permittivity in the frequency range of 8.2 to 12.4 GHz varied as a function of the PANI content in the blend. It was also observed that the compatibilizer agent increased the composite stiffness and decreased the electric permittivity values. This result shows that the increasing rigidity of the molecular structure of the polyethylene matrix hindered the dissipation of the electromagnetic energy in the sample.

Keywords: *Polyaniline, Polymer blends, High density polyethylene, Linear low density polyethylene, Electromagnetic properties*

1. Introduction

The electrically insulating and non-magnetic nature of polymers can be modified by the introduction of conducting and/or magnetic fillers into the polymers[1]. Thermally processed conducting polymer composites are more practical at industrial scale than solution processed systems. As a consequence, industrial-scale methods have been employed to produce conductive polymer composites. One way to obtain conducting polymer blends consists of mechanical dispersion of infusible conducting polymers in melt thermoplastic matrices to achieve conventionally moldable or extrudable conductive composites[2]. Among the conducting polymers, polyaniline (PANI) attracts great attention because of its chemical stability under ambient conditions, high electric conductivity, rather low cost, and simple synthesis[3-6]. Some researchers have reported that PANI doped and plasticized with dodecylbenzene sulfonic acid (DBSA)[7,8] and PANI protonated with phosphoric acid diester[9-11] exhibit excellent thermal and conductive properties. A PANI-DBSA complex can be blended with polyolefin matrices (polyethylene or polypropylene) in molten state. These polymer blends can be molded into antistatic or conductive films or even spun into fibers with a melt spinning technique[12,13].

Blends composed of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) have attracted considerable interest in both the research community and industry[14,15]. The advantages of the blends include, for example, improvements in impact strength, optical properties, low temperature impact strength, rheological properties, and overall mechanical behavior[16,17]. Mixtures of polyethylene and PANI have shown attractive properties such as antistatic behavior for gas separation materials, ion-exchange capacity for transducers in sensor devices, and electromagnetic-radiation-shielding and radar-absorbing materials (RAM, also called microwave absorbers) for electronic devices[18-20]. The miscibility between PANI and polyethylene is a critical issue and impacts on the composites' properties. In the case of melt mixing in extruders, the miscibility can be improved by the incorporation of disperser molecules such as compatibilizer agents, which can be added both as dopant molecules in PANI and as additives in the PANI-polyethylene mixture[2-5,20-22].

In our previous work[23], we studied the effect of the addition of PANI in LLDPE and observed an improvement in the electrical conductivity with the addition of PANI. Aiming to understand the effect of the branching of the polyethylene chain and the effect of the addition of compatibilizer agent on the electromagnetic properties, the purpose of this work is to obtain composites based on blends of HDPE and

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LLDPE with PANI doped with hydrochloric acid (HCl) by mixing in the molten state using a torque rheometer. The effect of the addition of compatibilizer agent (maleic anhydride-grafted high-density polyethylene, HDPE-g-MA) and different contents of PANI was also investigated. PANI was synthesized by the protonation method with HCl. The thermal, mechanical, morphological, and electromagnetic (8.2-12.4 GHz) properties of the HDPE/LLDPE/PANI blends with different contents of PANI were studied and correlated.

2. Experimental

2.1 Materials

The HDPE (DMDA 6200 NT-7) with a melt index of 0.38 g/10 min (190 ºC/2.16 kg) was supplied by Dow Chemical and the LLDPE (IC 32) with a melt index of 29 g/10 min (190 ºC/2.16 kg) was supplied by Braskem, Brazil. Processing of HDPE with a low melt index is difficult due to the high melt viscosity. The addition of a certain quantity of a material with a similar chemical structure and a high melt index, such as LLDPE facilitates the processing by reducing the melt viscosity and at the same time does not significantly change the properties of the more viscous matrix. The maleic anhydride-grafted high density polyethylene, HDPE-g-MA (Polybond® 3009), was supplied by Crompton Corporation. The HDPE and HDPE-g-MA were chosen because they have almost the same melt index [MI = 0.4 g / 10 min (190 ºC / 2.16 kg)].

PANI was synthesized using aniline (analytical grade, Vetec), which was distilled under vacuum and stored in a refrigerator, ammonium peroxydisulfate (Merck), and HCl (Vetec).

2.2 Polyaniline synthesis

PANI used in this work was synthesized following a well-established method for the synthesis of the emeraldine base form of PANI using HCl as dopant. In a typical polymerization, 5 mL of aniline was dissolved in 35 mL of distilled water under stirring. A solution of 5.71 g of ammonium peroxydisulfate (APS) in 100 mL of distilled water was added slowly, without stirring, to the aniline solution, followed by the rapid addition of 10 mL of 37% HCl. Polymerization was considered to have started at this point and was allowed to continue for 24 h at room temperature (25 ºC). The resulting dark-green solids were filtered and washed with hydrochloric acid and distilled water until the filtrate became colorless. Finally, the powder was dried in a vacuum oven at 60 ºC for 12 h.

2.3 Preparation of HDPE/LLDPE/PANI composites

All materials were dried for a minimum of 24 h in a vacuum oven at 80 ºC prior to melt processing. Composites of HDPE/LLDPE/PANI with a blend ratio of 1:1 (HDPE/LLDPE) and 5, 10, 15, 20, and 40 wt% PANI were prepared by melt compounding in a torque rheometer (Haake, model Rheomix 600p) using counter-rotational and interpenetrated rotors and operated at 180 ºC and 80 rpm for 4 min. In addition, compatibilized blends of HDPE/LLDPE/HDPE-g-MA/PANI with a blend ratio of 1:1 (HDPE:LLDPE), 15 wt% HDPE-g-MA, and 5, 10, 15, 20 and 40 wt% PANI were prepared under the same conditions. Table 1 shows the formulations prepared in this work. After processing, tensile tests probes were prepared by compression molding and stamping at 180 ºC for 3 min.

2.4 Thermal, mechanical, morphological, and electromagnetic characterization

Thermal characterization of HDPE/LLDPE/PANI composites was evaluated by differential scanning calorimetry (DSC; TA Instruments QS100) under an N_2 atmosphere. The measurements of the composites were performed according to the following procedures. The samples were heated from 200 ºC at 10 ºC/min, kept at this temperature for 5 min to erase any previous thermal history, and then cooled to 30 ºC at 10 ºC/min to determine the crystallization temperature (T_c). The melting point (T_m) was taken at the melting endothermic peak of the second heating cycle after erasing the thermal history. The degree of crystallinity of the blends (corrected for PANI content) was determined using the following equation: $X_c(\%) = (\Delta H_m / \Delta H_m^0 \times \phi_{blend}).100$, where ΔH_m is the enthalpy of melting measured by DSC; ΔH_m^0, the enthalpy of melting of 100% crystalline polymer, was taken as 292.6 J/g for HDPE, 140.6 J/g for LLDPE, and 290 J/g for HDPE-g-MA[24]; and Φ_{blend} is the volume fraction of blend in the composites. For the HDPE/LLDPE blends, the value of ΔH_m^0 used was 216.6 J/g, and for the HDPE/LLDPE/HDPE-g-MA, the value of ΔH_m^0 used was 227.6 J/g.

Mechanical properties were obtained by uniaxial tensile tests. Tensile tests were conducted on the molded specimens according to ASTM D638 using an Instron 5569 model at a crosshead speed of 50 $mm.min^{-1}$.

The fracture surface morphology of the composites was analyzed by SEM. The samples were covered with a thin layer of gold and the fracture surface was observed by scanning electron microscope (FEI Inspect S50) operated at 20 keV.

The electromagnetic characterization was performed by electric permittivity and magnetic permeability measurements. For this, specimens were cut to dimensions of 23 mm × 10 mm × 9 mm with the aid of a steel blade. The real and imaginary values of electric permittivity (ε) and magnetic permeability (μ) of the blends were obtained experimentally, in triplicate, through measures in a waveguide in the frequency range of 8.2 to 12.4 GHz (X-band). A vector network analyzer (model 8510C, HP) fitted with a calibration set for the X-band (type WR90) was used for this purpose. The calculation of the complex parameters ε and μ was carried out with the aid of the software 85017E (Agilent) based on the Nicolson Ross model[25]. The complex parameters ε and μ

Table 1. Detailed mass ratios of samples.

Sample	HDPE (wt%)	LLDPE (wt%)	PANI (wt%)	HDPE-g-MA (wt%)
HDPE/LLDPE (50/50)	50	50	---	---
HDPE/LLDPE/PANI (47.5/47.5/5)	47.5	47.5	5	---
HDPE/LLDPE/PANI (45/45/10)	45	45	10	---
HDPE/LLDPE/PANI (42.5/42.5/15)	42.5	42.5	15	---
HDPE/LLDPE/PANI (40/40/20)	40	40	20	---
HDPE/LLDPE/PANI (30/30/40)	30	30	40	---
HDPE/LLDPE/HDPE-g-MA (42.5/42.5/15)	42.5	42.5	---	15
HDPE/LLDPE/PANI/HDPE-g-MA (40/40/5/15)	40	40	5	15
HDPE/LLDPE/PANI/HDPE-g-MA (37.5/37.5/10/15)	37.5	37.5	10	15
HDPE/LLDPE/PANI/HDPE-g-MA (35/35/15/15)	35	35	15	15
HDPE/LLDPE/PANI/HDPE-g-MA (32.5/32.5/20/15)	32.5	32.5	20	15
HDPE/LLDPE/PANI/HDPE-g-MA (22.5/22.5/40/15)	22.5	22.5	40	15

are expressed by Equations 1 and 2, respectively, considering the real and imaginary components of the permittivity (ε', storage component; ε", loss component, respectively) and the permeability (μ' and μ", storage and loss components, respectively)[26].

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (1)$$

$$\mu = \mu' - j\mu'' \qquad (2)$$

3. Results and Discussion

3.1 Torque rheometer curves

Figure 1 shows the torque rheometer curves of the HDPE/LLDPE blends and the HDPE/LLDPE/PANI and HDPE/LLDPE/PANI/HDPE-g-MA with different contents of PANI, processed at 180 ºC and 80 rpm for 4 min. All components were mixed simultaneously. The torque peak corresponds to the addition of the compounds. A slight increase of the equilibrium torque was observed when the PANI content in the HDPE/LLDPE blends increased. The PANI does not melt in these processing conditions and the molten HDPE/LLDPE matrix involved the polyaniline particles during the processing. The composite obtained presented green coloration; however, a partial deprotonation and change of the doping degree can occur due to the poor stability of PANI at high temperatures. Similarly, the equilibrium torque increased with the addition of PANI in compatibilized composites. However, a greater increase in the equilibrium torque was observed in the compatibilized composites; that is, the addition of HDPE-g-MA promoted an increase in the interactions between HDPE and LLDPE and may also lead to an increase in interactions between the HDPE/LLDPE matrix and PANI. This is more evident for the composite with 40 wt% PANI, which presented an equilibrium torque of 9.5 N.m for HDPE/LLDPE/PANI (30/30/40) and 13.0 N.m for HDPE/LLDPE/PANI/HDPE-g-MA (22.5/22.5/40/15).

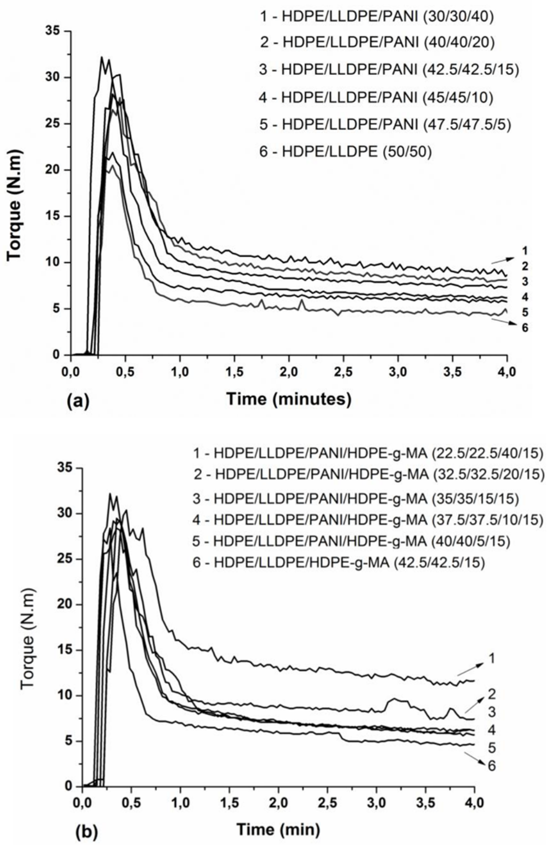

Figure 1. Variation of torque during mixing of the HDPE/LLDPE blends with different contents of PANI: (a) composites without compatibilizer agent and (b) compatibilized composites.

3.2 Thermal properties

Figure 2 shows the DSC thermograms for HDPE/LLDPE blend and HDPE/LLDPE/PANI composites with different contents of PANI. Table 2 summarizes the values of melting temperature (T_{m1} and T_{m2}) and melting enthalpy ($\Delta H_{m1\ and}\ \Delta H_{m2}$) obtained on the first and the second heating, respectively, and the values of crystallization temperature (T_c) obtained during the cooling scan, as well as the values of the degree of crystallinity for each composition. In all systems studied, only one crystallization temperature and one melting temperature peak were observed, indicating the existence of only one type of crystal species in these compositions. These results may be indicative of the miscibility of the system and the fact that co-crystallization took place in the HDPE/LLDPE blend. On the other hand, polyethylenes (HDPE and LLDPE) and PANI are immiscible due to the significant differences in the polarities of these polymers and it was observed that the addition of PANI in the blends does not affect the T_m and T_c values. However, the increase of PANI content in the composites causes a reduction in the degree of crystallinity of HDPE/LLDPE blend, which implies that the PANI particles make the co-crystallization of HDPE and LLDPE difficult.

Figure 3 shows the DSC thermograms for HDPE/LLDPE/HDPE-g-MA blends and HDPE/LLDPE/PANI/HDPE-g-MA composites with different contents of PANI and Table 3 summarizes the thermal properties.

The addition of compatibilizer agent in the HDPE/LLDPE blend increased the degree of crystallinity. For systems with 5, 10, 15, and 20 wt% PANI, no change in the degree of crystallinity was observed. However, the addition of 40 wt% PANI in the blend led to a significant decrease in the degree of crystallinity (about 10%). For this composition, the decrease may be attributed to the higher interfacial adhesion between the HDPE-g-MA and PANI, which can reduce the mobility of crystallized chain segments.

3.3 Mechanical properties

Table 4 presents the values of tensile stress at break (σ_b), elongation at break (ε_b), and Young's modulus (E) obtained by uniaxial tensile tests. The addition of PANI impacted on the mechanical behavior of the HDPE/LLDPE blend, promoting a substantial reduction in elongation at break, and brittle fracture was observed as the content of PANI in the composites increased. The PANI is polar and the polyethylene matrix is nonpolar; it can be assumed that there is a lack of adhesion between the different phases and that the mechanical properties of the polymer matrix are negatively affected by the addition of PANI. On the other hand, the addition of the compatibilizing agent (HDPE-g-MA) increased the Young´s modulus of the HDPE/LLDPE/PANI composites with different contents of PANI. These results suggest that the compatibilizer agent increases the interfacial adhesion between HDPE/LLDPE and polyaniline and contributes

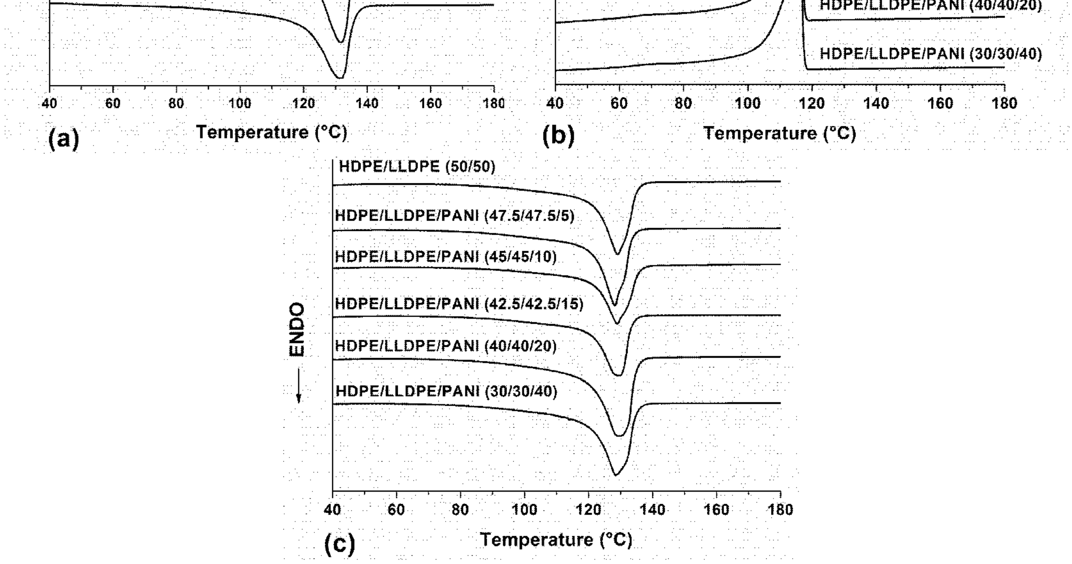

Figure 2. DSC thermograms of HDPE/LLDPE/PANI composites with different contents of PANI: (a) first heating, (b) cooling, and (c) second heating.

Table 2. Values of Tm, ΔH_m, and X_c obtained during heating scans and T_c obtained during cooling scans of HDPE/LLDPE/PANI composites.

Sample	T_{m1} (°C)	ΔH_{m1} (J/g)	Xc_1 (%)	T_c (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_{c2} (%)
HDPE/LLDPE (50/50)	132	137.5	63.5	114	129	146.4	67.6
HDPE/LLDPE/PANI (47.5/47.5/5)	132	136.2	66.2	115	129	138.5	67.3
HDPE/LLDPE/PANI (45/45/10)	131	121.0	62.0	115	129	130.5	67.0
HDPE/LLDPE/PANI (42.5/42.5/15)	129	114.2	62.0	116	129	119.4	64.8
HDPE/LLDPE/PANI (40/40/20)	132	107.6	62.1	115	129	107.5	62.0
HDPE/LLDPE/PANI (30/30/40)	131	81.5	62.7	114	129	78.9	60.7

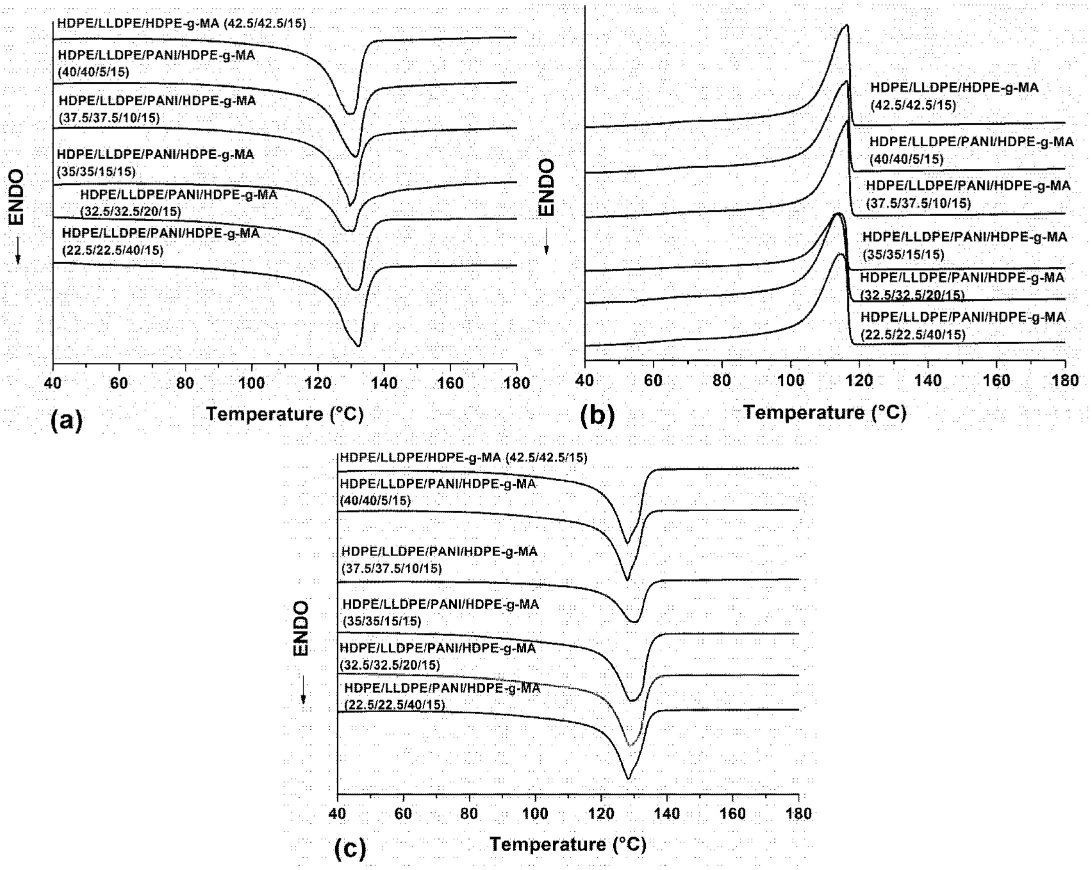

Figure 3. DSC thermograms of HDPE/LLDPE/PANI blends with different contents of PANI: (a) first heating, (b) cooling, and (c) second heating.

Table 3. Values of Tm, ΔHm and Xc obtained during heating scans and T_c obtained during cooling scans of HDPE/LLDPE/PANI/HDPE-g-MA composites.

Sample	T_{m1} (°C)	ΔH_{m1} (J/g)	Xc_1 (%)	T_c (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	Xc_2 (%)
HDPE/LLDPE/HDPE-g-MA (42.5/42.5/15)	132	151.3	66.4	115	129	160.3	70.4
HDPE/LLDPE/PANI/HDPE-g-MA (40/40/5/15)	131	143.4	66.4	116	129	145.9	67.5
HDPE/LLDPE/PANI/HDPE-g-MA (37.5/37.5/10/15)	130	131.2	63.6	116	128	139.1	67.4
HDPE/LLDPE/PANI/HDPE-g-MA (35/35/15/15)	131	119.0	60.9	116	128	130.1	67.2
HDPE/LLDPE/PANI/HDPE-g-MA (32.5/32.5/20/15)	130	110.3	60.6	116	128	124.1	67.2
HDPE/LLDPE/PANI/HDPE-g-MA (22.5/22.5/40/15)	130	75.5	55.3	113	130	81.1	57.4

Table 4. Tensile stress at break (σb), Young's modulus (E), and elongation at break (er) obtained in the uniaxial tensile test.

Sample	σ_b (MPa)	E (GPa)	ε_r (%)
HDPE/LLDPE (50/50)	---	0.85 ± 0.04	> 300
HDPE/LLDPE/PANI (47.5/47.5/5)	14.5 ± 0.9	0.70 ± 0.03	10.5 ± 1.4
HDPE/LLDPE/PANI (45/45/10)	13.1 ± 0.5	0.75 ± 0.04	8.7 ± 1.4
HDPE/LLDPE/PANI (42.5/42.5/15)	12.2 ± 0.7	0.81 ± 0.13	3.7 ± 0.4
HDPE/LLDPE/PANI (40/40/20)	11.4 ± 1.0	0.84 ± 0.10	3.1 ± 0.1
HDPE/LLDPE/PANI (30/30/40)	8.7 ± 0.3	0.88 ± 0.02	1.7 ± 0.4
HDPE/LLDPE/HDPE-g-MA (42.5/42.5/15)	12.6 ± 1.2	0.83 ± 0.04	82.1 ± 7.8
HDPE/LLDPE/PANI/HDPE-g-MA (40/40/5/15)	16.6 ± 1.0	0.86 ± 0.09	12.0 ± 1.7
HDPE/LLDPE/PANI/HDPE-g-MA (37.5/37.5/10/15)	16.7 ± 0.4	0.95 ± 0.02	7.8 ± 1.2
HDPE/LLDPE/PANI/HDPE-g-MA (35/35/15/15)	15.5 ± 0.8	0.97 ± 0.03	3.8 ± 1.0
HDPE/LLDPE/PANI/HDPE-g-MA (32.5/32.5/20/15)	14.9 ± 1.2	0.96 ± 0.03	3.4 ± 0.1
HDPE/LLDPE/PANI/HDPE-g-MA (22.5/22.5/40/15)	8.0 ± 1.0	0.99 ± 0.01	1.3 ± 0.3

to an increase in stiffness of the final composite. The use of HDPE-g-MA in the composite structure leads to better compatibility with HDPE, so composites with good mechanical properties were obtained with only a mixing procedure and without the addition of any dispersant. Del Castillo-Castro *et al.*[18] studied the influence of the compatibilization of polyethylene-graft-maleic anhydride (PE-g-MA) in composites of low-density polyethylene (LDPE) and n-dodecylbenzene sulfonate doped polyaniline (PANI-DBSA) prepared by extrusion. The authors reported results similar to those obtained in the present study and attributed the improvement in the mechanical properties to the use of compatibilizers as interfacial agents in composites.

3.4 Morphology

The fracture surface morphologies of the HDPE/LLDPE/PANI blends with different contents of PANI are shown in Figure 4. It is verified that all the fracture surface micrographs show distinct morphologies, which are influenced by the increased contents of PANI in the HDPE/LLDPE blends. Figure 4a, which is related to HDPE/LLDPE blend containing 5 wt% PANI, shows a surface with small ridges and ripples in the whole of the sample. However in Fig. 4b-d, the blend samples clearly show irregularly shaped PANI lumps with rough surfaces dispersed in the HDPE/LLDPE continuous phase.

The SEM image of the composite with a higher content of PANI (40 wt%) (Fig. 4e) shows a rough morphology with the presence of aggregates of PANI and distinct phase boundaries between the HDPE/LLDPE matrix and PANI, which are specified by white arrows. These morphological aspects indicate a weak adhesion between the phases, indicating poor interfacial adhesion between HDPE/LLDPE and PANI.

According to Nand et al.[27], this behavior is attributed to the dissimilarity in the polarity of the polymers: while HDPE and LLDPE are typical non-polar hydrocarbon polymers, PANI possesses high polarity due to the presence of amine groups in its macromolecular structure.

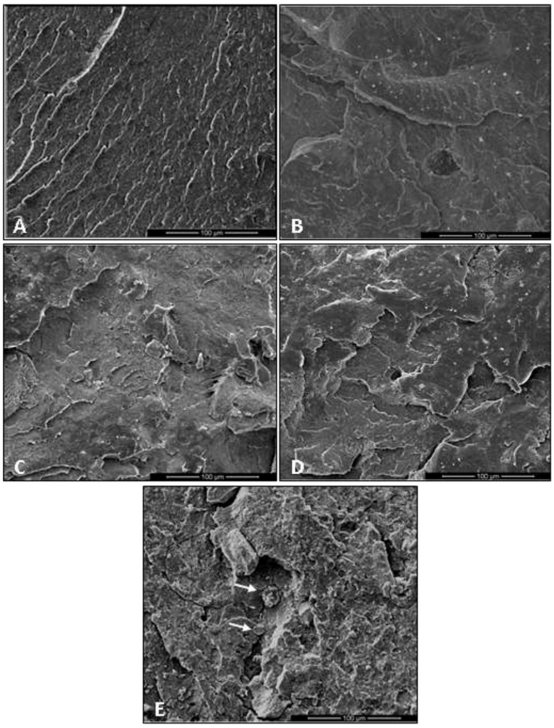

Figure 4. SEM micrographs of fractured surfaces of (a) HDPE/LLDPE/PANI (47,5/47,5/5), (b) HDPE/LLDPE/PANI (45/45/10), (c) HDPE/LLDPE/PANI (42,5/42,5/15), (d) HDPE/LLDPE/PANI (40/40/20), and (e) HDPE/LLDPE/PANI (30/30/40), with magnification of 1000×.

The fracture surface morphologies of the HDPE/LLDPE/HDPE-g-MA/PANI composites with different contents of PANI are shown in Figure 5. It is possible to observe that all the composites present more homogeneous and flat fracture surfaces. The compositions with high contents of PANI present slight undulations in the micrographs, and this observation suggests that the compatibilizing agent present in the composition of the HDPE/LLDPE/PANI composites increased the homogeneity of the PANI dispersion and conferred the fragile aspect on the final composite. Consequently, the maleic anhydride compatibilizing agent induced changes in both the morphology of the composites and the interfacial adhesion/matrix domains, which influenced the mechanical properties; that is, it contributed to the stiffness increase of the material. The presence of functional groups (HDPE-g-MA) on the backbone of the matrix caused good interaction between it and PANI, leading to good dispersion of PANI in the matrix of the HDPE/LLPE/HDPE-g-MA.

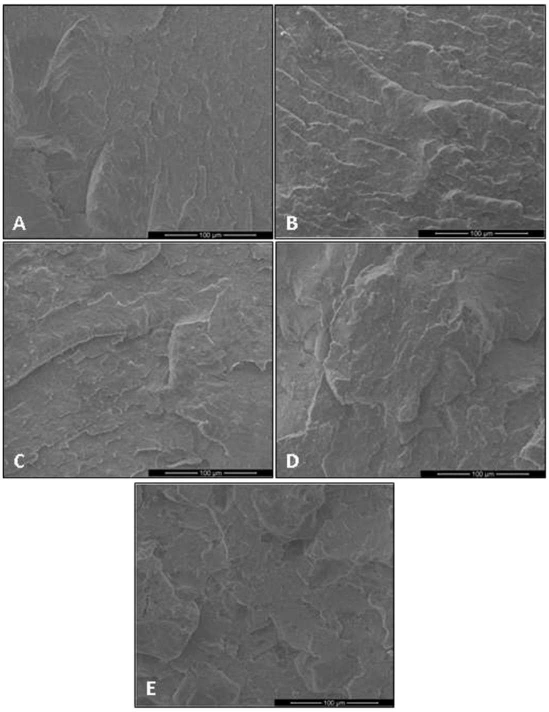

Figure 5. SEM micrographs of fractured surfaces of (a) HDPE/LLDPE/PANI/HDPE-gMA (40/40/5/15), (b) HDPE/LLDPE/PANI/HDPE-g-MA (37,5/37,5/10/15), (c) HDPE/LLDPE/PANI/HDPE-g-MA (35/35/15/15), (d) HDPE/LLDPE/PANI/HDPE-g-MA (32,5/32,5/20/15), and (e) HDPE/LLDPE/PANI/HDPE-g-MA (22,5/22,5/40/15), with magnification of 1000×.

Quiroz-Castillo et al.[28] studied the influence of the addition of polyethylene-graft-maleic anhydride as compatibilizer for blends of LDPE and glycerol. The authors noted that the use of compatibilizer and plasticizer agents improved the processability and compatibility of the mixtures, as well their mechanical properties, as revealed by mechanical property measurements and SEM.

3.5 Electromagnetic characterization

Figure 6 shows typical graphs of ε' as a function of frequencies in the X-band (8.2 to 12.4 GHz) of the studied samples. Firstly, it is observed that HDPE/LLDPE and HDPE/LLDPE/HDPE-g-MA matrices (without PANI) presented the lowest values of ε', 2.098 and 2.053, at 10 GHz, respectively (Table 5). Table 5 presents the complex parameters of ε in the middle of the X-band, that is, at 10 GHz. It is also verified that the ε' of the HDPE/LLDPE matrix containing the HDPE-g-MA agent is slightly smaller. It is observed that ε' increases progressively, with values of 3.142, 3.956, and 4.828 at 10 GHz for the HDPE/LLDPE/PANI containing 10, 15, and 20 wt% PANI, respectively. The highest value of 13.518 was observed for the composite with 40 wt% PANI. The presented behavior is attributed to the electrical conductivity of PANI[29], where the increment of PANI favored the increment of the storage component of the electric permittivity of the composites, with a maximum value for the sample containing 40 wt% PANI. Figure 6b shows the ε' curves for HDPE/LLDPE/PANI/HDPE-g-MA samples. Compared to HDPE/LLDPE/PANI, the samples containing the compatibilizer agent show lower ε' values (varying from 2.658 up to 11.528). The correlation of this electromagnetic parameter with the mechanical properties shows that the HDPE-g-MA increased the molecular rigidity of the composites and disfavored the electromagnetic radiation interaction; that is, stiffer molecular structures resulted in lower ε' values. The graphs also show that ε' exhibits a slight decrease with increasing frequency. Similar behavior is described in the literature[30,31].

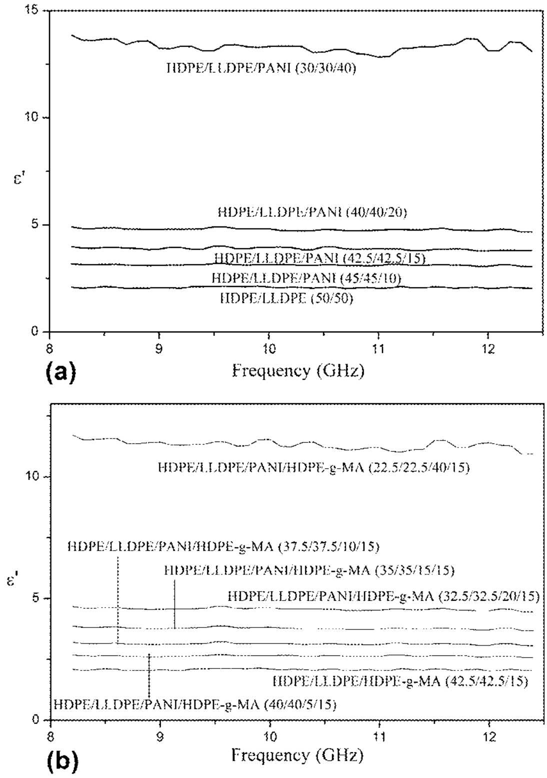

Figure 6. Graphs of ε' *versus* frequency of (a) LLDPE/HDPE/PANI and (b) LLDPE/HDPE/PANI/HDPE-g-MA.

Figure 7 shows the analysis of the loss component (ε"), which presented more significant variations as a function of the frequency but, comparatively, it is possible to see that the increment of PANI in the HDPE/LLDPE/PANI

Table 5. Complex parameters of of the LLDPE/HDPE/PANI and LLDPE/HDPE/PANI/HDPE-g-MA samples at 10 GHz.

Sample	**ε'**	**ε''**
HDPE/LLDPE	2.098	0.010
HDPE/LLDPE/PANI (45/45/10)	3.142	0.037
HDPE/LLDPE/PANI (42.5/42.5/15)	3.956	0.058
HDPE/LLDPE/PANI (40/40/20)	4.828	0.069
HDPE/LLDPE/PANI (30/30/40)	13.518	1.805
HDPE/LLDPE/HDPE-g-MA (42.5/42.5/15)	2.053	0.015
HDPE/LLDPE/PANI/HDPE-g-MA (40/40/5/15)	2.658	0.024
HDPE/LLDPE/PANI/HDPE-g-MA (37.5/37.5/10/15)	3.163	0.034
HDPE/LLDPE/PANI/HDPE-g-MA (35/35/15/15)	3.817	0.050
HDPE/LLDPE/PANI/HDPE-g-MA (32.5/32.5/20/15)	4.630	0.068
HDPE/LLDPE/PANI/HDPE-g-MA (22.5/22.5/40/15)	11.528	0.953

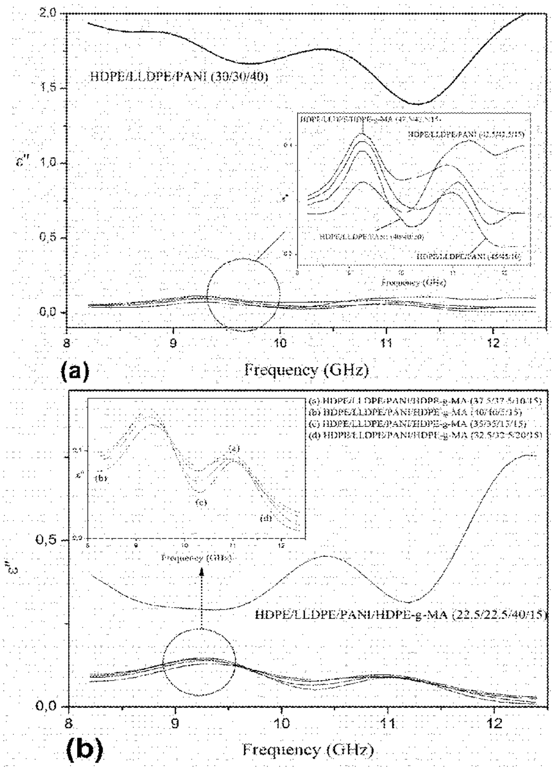

Figure 7. Graphs of ε'' *versus* frequency of (a) LLDPE/HDPE/PANI and (b) LLDPE/HDPE/PANI/HDPE-g-MA.

composites increases the losses. This behavior is attributed to the electric conductivity of PANI[29]. The highest ε'' values are observed for the samples containing 40 wt% PANI in the composites with and without compatibilizer agent (0.953 and 1.805, respectively, Table 5). In this case, the presence of HDPE-g-MA diminishes the losses probably due to the higher rigidity of the molecular structure containing the compatibilizing agent.

In a general way, the complex parameters of permittivity show that the composites present a stronger capacitive effect, storing energy but with low dissipation. This fact is enhanced in samples containing HDPE-g-MA agent, which may be attributed to the possible increase of the stiffness of the polyethylene matrix, disfavoring the losses of incident waves in the X-band.

The magnetic parameters μ' and μ'' varied around 1 and 0, respectively, for all samples. These values are typical for dielectric materials, as cited in the literature[32].

4. Conclusions

PANI affects the thermal, mechanical, and electromagnetic properties of HDPE/LLDPE blends. The increase of PANI content in the polymer blends reduces the degree of crystallinity and increases the Young´s modulus and the complex parameters of electric permittivity. This indicates that there is good adhesion between the HDPE/LLDPE and PANI. The addition of HDPE-g-MA compatibilizer agent affects the properties of the HDPE/LLDPE/PANI blends, increasing the interactions between HDPE/LLDPE matrix and PANI and enhancing the stiffness of the composites. The fracture surface analysis shows that the presence of compatibilizer agent in the HDPE/LLDPE/PANI improved the homogeneity and the dispersion of the PANI particles in the composites, resulting in a more fragile fracture surface. The presence of PANI in the composites increased the complex parameters of electric permittivity due to its electric conductivity, but this increment is less pronounced in the composites with the compatibilizer agent due to the greater stiffness of the polyethylene matrix, which disfavored the interaction and the dissipation of electromagnetic radiation in the composites.

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6. References

1. Mezdour D, Tabellout M, Sahli S, Fateyeyeva K. Electrical Properties Investigation in PA12/PANI Composites. *Macromolecular Symposia*. 2010;290(1):15-24.

2. Pud A, Ogurtsov N, Korzhenko A, Shapoval G. Some aspects of preparation methods and properties of polyaniline blends and composites with organic polymers. *Progress in Polymer Science*. 2003;28(12):1701-1753.

3. Haba Y, Segal E, Narkis M, Titelman GI, Siegmann A. Polyaniline-DBSA/polymer blends prepared via aqueous dispersions. *Synthetic Metals*. 2000;110(3):189-193.

4. Annala M, Löfgren B. Compatibilization of Conductive Polyethylene/Polyaniline Blends. *Macromolecular Materials and Engineering*. 2006;291(7):848-857.

5. Bhattacharya A, De A. Conducting composites of polypyrrole and polyaniline: a review. *Progress in Solid State Chemistry*. 1996;24(3):141-181.

6. Bouanga CV, Fateyeyeva K, Baillif PY, Bardeau JF, Khaokong C, Pillard JF, et al. Study of dielectric relaxation phenomena and electrical properties of conductive polyaniline based composite films. *Journal of Non-Crystalline Solids*. 2010;356(11-17):611-615.

7. Passiniemi P, Laakso J, Österholm H, Pohl M. TEM and WAXS characterization of polyaniline/PP fibers. *Synthetic Metals*. 1997;84(1-3):775-776.

8. Laska J, Pron A, Zagórska M, Lapkowski S, Lefrant S. Thermally processable conducting polyaniline. *Synthetic Metals*. 1995;69(1-3):113-115.

9. Wang XH, Geng YH, Wang LX, Jing XB, Wang FS. Thermal behaviors of intrinsic polyaniline and its derivatives. *Synthetic Metals*. 1995;69(1-3):263-264.

10. Haba Y, Segal E, Narkis M, Titelman GI, Siegmann A. Polymerization of aniline in the presence of DBSA in an aqueous dispersion. *Synthetic Metals*. 1999;106(1):59-66.

11. Laughlin PJ, Monkman AP. Mechanical properties of oriented emeraldine base polyaniline. *Synthetic Metals*. 1997;84(1-3):765-766.

12. Laska J, Pron A, Lefrant S. Phosphoric acid diesters protonated polyaniline: Preparation, spectroscopic properties, and processability. *Journal of Polymer Science Part A: Polymer Chemistry*. 1995;33(9):1437-1445.

13. Zhang Q, Wang X, Geng Y, Chen D, Jing X. Morphology and thermal properties of conductive polyaniline/polyamide composite films. *Journal of Polymer Science Part B: Polymer Physics*. 2002;40(22):2531-2538.

14. Liu C, Wang J, He J. Rheological and thermal properties of m-LLDPE blends with m-HDPE and LDPE. *Polymer*. 2002;43(13):3811-3818.

15. Choi P. Molecular dynamics studies of the thermodynamics of HDPE/butene-based LLDPE blends. *Polymer*. 2000;41(24):8741-8747.

16. Hussein IA. Influence of Composition Distribution and Branch Content on the Miscibility of m-LLDPE and HDPE Blends: Rheological Investigation. *Macromolecules*. 2003;36(6):2024-2031.

17. Quental AC, Felisberti MI. Phase behavior of blends of linear low density polyethylene and poly (ethene-propene-1-butene). *European Polymer Journal*. 2005;41(5):894-902.

18. Del Castillo-Castro T, Castillo-Ortega MM, Herrera-Franco PJ, Rodríguez-Félix DE. Compatibilization of polyethylene/polyaniline blends with polyethylene-graft-maleic anhydride. *Journal of Applied Polymer Science*. 2011;119(5):2895-2901.

19. Elyashevich GK, Kozlov AG, Gospodinova N, Mokreva P, Terlemezyan L. Combined polyethylene-polyaniline membranes. *Journal of Applied Polymer Science*. 1997;64(13):2665-2666.

20. Boon MS, Serena Saw WP, Mariatti M. Magnetic, dielectric and thermal stability of Ni-Zn ferrite-epoxy composite thin films for electronic applications. *Journal of Magnetism and Magnetic Materials*. 2012;324(5):755-760.

21. Heeger AJ. Polyaniline with surfactant counterions: Conducting polymer materials which are processible in the conducting form. *Synthetic Metals*. 1993;57(1):3471-3482.

22. Bhadra S, Khastgir D, Singha NK, Lee JH. Progress in preparation, processing and applications of polyaniline. *Progress in Polymer Science*. 2009;34(8):783-810.

23. Passador FR, Faria PV, Backes EH, Montanheiro TLA, Montagna LS, Pinto SS, et al. Thermal, mechanical and electromagnetic properties of LLDPE/PANI composites. *Polymer Bulletin*. 2017;74(7):2701-2717. DOI: 10.1007/s00289-016-1862-5

24. Wunderlich B. *Macromolecular Physics*. New York: Academic Press; 1980.

25. Nicolson AM, Ross GF. Measurement of the Intrinsic Properties of Materials by Time-Domain Techniques. *IEEE Transactions on Instrumentation and Measurement*. 1970;19(4):377-382.

26. Gama AM, Rezende MC, Dantas CC. Dependence of microwave absorption properties on ferrite volume fraction in MnZn ferrite/rubber radar absorbing materials. *Journal of Magnetism and Magnetic Materials*. 2011;323(22):2782-2785.

27. Nand AV, Ray S, Travas-Sejdic J, Kilmartin PA. Characterization of antioxidant low density polyethylene/polyaniline blends prepared via extrusion. *Materials Chemistry and Physics*. 2012;135(2-3):903-911.

28. Quiroz-Castillo JM, Rodríguez-Félix DE, Grijalva-Monteverde H, del Castillo-Castro T, Plascencia-Jatome M, Rodríguez-Félix F, et al. Preparation of extruded polyethylene/chitosan blends compatibilized with polyethylene-*graft*-maleic anhydride. *Carbohydrate Polymers*. 2014;101:1094-1100.

29. Müller F, Ferreira CA, Amado FDR, Rodrigues MAS. Desenvolvimento de membranas e filmes auto-suportados a partir de polianilina: síntese, caracterização e aplicação. *Polímeros*. 2011;21(4):259-264.

30. Kao KC. *Dielectric Phenomena in Solids*. New York: Academic Press; 2004.

31. Pradhan DK, Choudhary RNP, Samantaray BK. Studies of Dielectric Relaxation and AC Conductivity Behavior of Plasticized Polymer Nanocomposite Electrolytes. *International Journal of Electrochemical Science*. 2008;3:597-608.

32. Wu KH, Ting TH, Wang GP, Ho WD, Shih CC. Effect of carbon black content on electrical and microwave absorbing properties of polyaniline/carbon black nanocomposites. *Polymer Degradation and Stability*. 2008;93(2):483-488.