Polyaniline Synthesized with Functionalized Sulfonic Acids for Blends Manufacture

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Polyaniline (PAni), an electronic conductive polymer, has poor mechanical properties, such as low tensile, compressive and flexural strength that render PAni a non-ideal material to be processed for practical applications. Desired properties of polyaniline can be enhanced by mixing it with a polymer that has good mechanical properties. In this work, PAni was synthesised using functionalized sulfonic acids like camphorsulfonic acid (CSA) and dodecilbenzene sulfonic acid (DBSA) in order to promote PAni doping and improve its solubility, making possible conductive blends manufacture. The different forms of PAni were characterized by infra-red spectroscopy, thermal analysis, scanning electron microscopy and conductivity measurements. A conductive blend composed of PAni/DBSA and lower density polyethylene (LDPE) was obtained via solubilization method and its thermal, morphological and electrical properties were investigated. Concentrations as low as 5 wt. (%) of PAni was able to lead to electrical conductivities of PAni/LDPE blends in the range of 10^{-3} S.cm^{-1}, showing great potential to be used in antistatic packing, electromagnetic shielding, anti-corrosion shielding or as a semiconductor.

Keywords: *polyaniline, lower density polyethylene, conductive blends*

1. Introduction

Electronic conductive polymers (ECP) have been the subject of study as possible organic metals. Many of these polymers often yield higher conductivity once having undergone the doping process. However, the main disadvantage of ECP is their poor mechanical properties such as strength and processability due to stiffness of their backbone. Thus, the unique combination of electronic and mechanical properties of ECP blends with conventional polymers seems to have great promise for many applications[1-3]. The mixing of polymers has become commercially and technologically more important than the synthesis of homopolymers and copolymers in the last decade. Blending allows creating new materials with specific properties for the desired application at low cost. Since the conducting polyblends are stable and retain the mechanical properties of the host polymer, films, fibers, and coatings can be fabricated by solvent evaporation or by melt-processing for use in anti-static applications, for electromagnetic shielding, microwave absorption devices and/or for transparent conducting films[4].

In polyaniline (PAni), an electrically conductive polymer, a conjugated double bond structure composed by the benzenoid ring between the quinoid imine and the benzenoid amine structures (Figure 1) form the conjugation π-bond system[5]. The conjugated double bonds permit easy electron mobility throughout the molecule due to electrons delocalization. Among the three oxidation states of PAni, only doped emeraldine-based (EB) form, being a partially reduced and partially oxidized form, is conductive.

According to MacDiarmid et al.[6], doping is the process by which polymers that are insulators are exposed to charge transfer agent (dopant). PAni is the only conducting polymer whose properties not only depend on the oxidation state but also on its protonation state/doping level and also on the nature of dopants. The electrical conductivity of undoped PAni is reported to be in the range of 10^{-10} to 10^{-7} S.cm^{-1}. Upon acid doping it attains higher values in the range of 10^{-2} to 100 S.cm^{-1}, depending on the dopant. PAni doping with acids improves conductivity levels forming polaron/bipolaron struc-

tures that will increase PAni's charge due to the increased electronic delocalization.

Thus, ECP are better semiconductors alternatives to the conventional inorganic such as silicon and bismuth arsenate. The disadvantages of conducting polymers arise from the fact that they are not highly stable compounds even at moderate temperatures (>150 °C) and the most of them exhibit dark colour due to their highly oxidized states, besides their insolubility in the common organic solvents. In order to overcome the above-mentioned drawbacks, it is essential to blend conducting polymers with conventional polymers[7]. Although blending of PAni with other polymers leads to a decrease in its electrical conductivity, it is conceivable that composites or blends with moderate conductivity and good mechanical properties can be obtained by the blending approach[8].

In this work, conductive blends composed by PAni and low density polyethylene (LDPE) were manufactured via solubilization method. For this purpose, functionalized sulfonic acids in aqueous oxidizing medium were tested as dopants of PAni in order to study their influence in PAni conductivity and solubility. PAni and PAni/LDPE blend were characterized by scanning electron microscopy, thermal analysis and conductivity measurements. Besides, infra-red spectroscopy was used to identify the conductive bands for PAni samples.

2. Materials and Methods

2.1. Synthesis and characterization of PAni

The monomer aniline (Merck) was freshly distilled prior to use. After, 0.5 M aniline was chemically polymerized in 1 M HCl solution using ammonium persulphate ($(NH_4)_2S_2O_8$) as oxidizing agent. The polymerization reaction was kept between 0 and 5 °C for two hours. The ammonium persulphate concentration was related to aniline concentration by the K parameter, as described in work of Prón et al.[9] and Lenz et al.[10]. A low value of K parameter means oxidizing agent
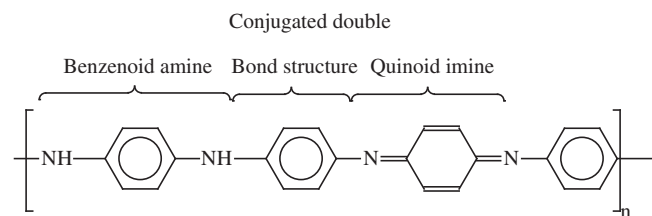
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Conjugated double

Benzenoid amine   Bond structure   Quinoid imine

Figure 1. Chemical structure of dedoped PAni (emeraldine-base form).

Table 1. Solubility Degree and Conductivity for different forms of PAni.

	Solubility degree		
	in Toluene 90 °C (%)	in THF 45 °C (%)	Conductivity* (S.cm^{-1})
PAni/ CSA	25	35	0.8
PAni/ DBSA	30	40	1.0
PAni/HCl	9	16	3.0
PAni/NaOH	20	33	Below 10^{-6}

*polimerization reactions carried out with K parameter value = 0.8 at 0-5 °C for 2 hours using $(NH_4)_2S_2O_8$ as oxidant agent.

number of mols in excess with respect to aniline number of mols. PAni powder was then washed and dried. The PAni doped with HCl acid is called PAni/HCl. Afterwards, PAni/HCl powder was neutralized with 0.1 M NaOH for 24 hours in order to obtain PAni in the dedoped state (insulator state), called PAni/NaOH. Finally, a doping process was performed in PAni/NaOH using a functionalized sulfonic acid: 1 M dodecil benzenesulfonic acid (DBSA), yielding PAni/DBSA, or 1 M camphorsulfonic acid (CSA), yielding PAni/CSA samples.

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the specific bands of the different forms of PAni with a FTIR Perkin Elmer spectrophotometer. PAni morphology was investigated using a Philips XL 20 scanning electron microscope and conductivity measurements were carried out at room temperature, following the four probe technique[11], with a RD2 differential resistometer. Solubility measurements of PAni samples were carried out using organic solvents as toluene and tetrahidrofurane (THF). Thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) were also used to characterize the different forms of PAni. Thermal studies of PAni are particularly important when one considers the use of elevated temperatures to process PAni and its blends into technologically useful forms. Thermogravimetric analysis (TGA) was performed in a TG2050 thermal analyser in order to find the decomposition temperature of PAni compounds. PAni samples were scanned from 0 to 1000 °C at a scanning rate of 20 °C/min under nitrogen gas purging. DSC was performed using a DSC 2010 differential scanning calorimeter. For DSC experiments, each sample was heated from 30 to 240 °C at 10 °C/min.

2.2. Blends manufacture and characterization

A PB - 681 low density polyethylene (LDPE) from Braskem (Pólo Petroquímico de Triunfo - RS) was used for blends manufacture. PAni/DBSA and LDPE were dissolved in toluene at 90 °C under magnetic stirring to form a homogeneous mixture which was cast in glass petri-dish. Blends of LDPE and 1, 2, 5, 10 and 20 wt. (%) PAni/DBSA were obtained from the solution by slow solvent evaporation in vacuum stove in order to investigate blend conductivity as function of PAni concentration. Blends were pressed in pellets form in a hydraulic press applying 15 kN/m^2 for 10 minutes at room temperature to measure blends conductivity using the four probe method. Further, blends morphology was investigated using scanning electron microscopy. In addition, the thermal properties were evaluated using a TG2050 thermal analyzer equipment from TA Instruments.

3. Results and Discussion

3.1. Synthesis and characterization of PAni

Concerning the polymerization reaction, higher the K parameter value is, lower is the reaction yield, however PAni conductivity increase. Thus, using a parameter K value of 0.8, PAni/HCl samples showed an average conductivity of 3 S.cm^{-1} (Table 1) with 98% of reaction yield while PAni/HCl samples synthesized using a K value

of 6 showed a conductivity increase to around 15 S.cm^{-1}. Nevertheless, the reaction yield dropped to only 6%.

In Table 1, the results of PAni solubility experiments can be also found. Although its high conductivity, PAni/HCl has poor solubility in common organic solvents. PAni/DBSA and PAni/CSA showed higher degree of solubility in toluene and THF, making possible blending PAni with other polymers, in agreement with recent works[12,13]. Besides, all forms of PAni were more soluble in THF than in toluene. However, LDPE is weakly soluble in this solvent. Thus, toluene was considered the appropriate solvent for PAni/ LDPE blends manufacture. PAni/DBSA synthesized in operational conditions described in Table 1 (K parameter value equal to 0.8 at 0-5 °C for 2 hours using $(NH_4)_2S_2O_8$ as oxidant agent) was also chosen for blends manufacture since PAni/DBSA is the form of PAni that showed the highest solubility degree in both THF and toluene.

In FTIR analysis, there were no significant changes in the bands of PAni doped with dopant agents like HCl, DBSA or CSA. The analysis of the functional groups of PAni/HCl and PAni/DBSA by FTIR spectroscopy (Figure 2) showed structural characteristics similar to those reported by Freitas[12]. The main bands are situated around de 820 cm^{-1} (C-H out-of-plane bending vibration in the 1,4 disubstituted ring), around 1140 cm^{-1} (vibrational band of the quinoid N – the electronic band attributed due to charge delocalization on the polymer), in the range of 1240 - 1300 cm^{-1} (C-N stretching of the aromatic secondary amines), around 1500 cm^{-1} (benzenoid stretching) and around 1600 cm^{-1} (quinoid stretching).

TGA was used in order to find the decomposition temperature of PAni. This important temperature sets an upper boundary for the temperature at which PAni can be heated for subsequent works. Figure 3 shows the thermograms for the different forms of PAni. PAni/DBSA started to degrade in lower temperature (around 250 °C) with respect to other forms of PAni. This fact was also observed by Freitas[12]. For PAni/NaOH, the TGA curve showed the decomposition beginning at around 500 °C, while for PAni/HCl the decomposition temperature was above 400 °C, after water and HCl loss.

The acid-doped forms of PAni showed a three step decomposition process, as proposed by previous workers[14]. They suggest that the initial stages of weight loss are due to the volatilization of water molecules and oligomers, as well as unreacted monomer elimination. Then, at higher temperatures the protonic acid component of the polymer is lost and finally at more extreme temperatures the polymer chain break can lead to production of gases such as acetylene and ammonia. PAni/HCl was found to be the more thermally stable with respect to PAni/DBSA since the later form showed higher weight losses before the thermal breakdown of the polymer backbone. Emeraldine-base form (PAni/NaOH) showed after water loss almost a straight line up to its decomposition onset.

DSC curves (Figure 4) for the same forms of PAni showed endothermic peaks: around 130 °C for PAni/NaOH and PAni/HCl and around 145 °C for PAni/DBSA. These endothermic transitions

are related to the water excess and they are dislocated with respect to TGA experiments since DSC experiments were performed with hermetic pans. The water influence on the polymer crystal structure is poorly studied. Freitas[12] suggested that water can even be bound to the PAni lattice and Lubentsov et al.[15] concluded that water influences the crystal structure of PAni and thus changes its conductivity.
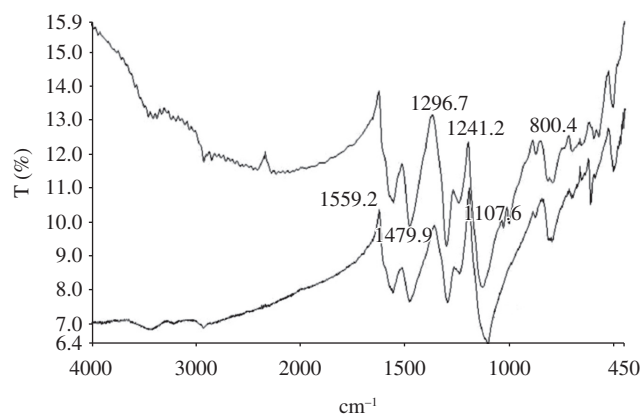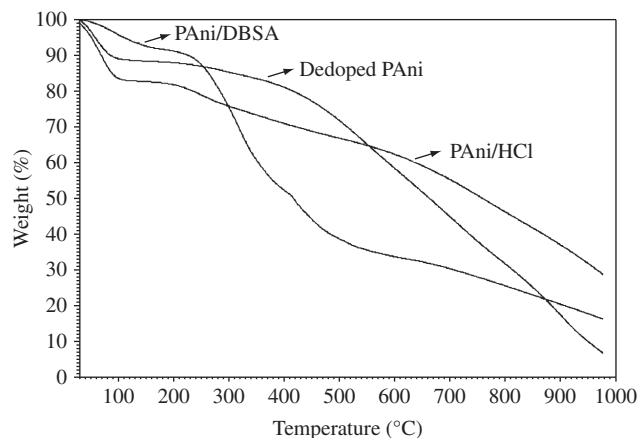

Figure 2. FTIR spectra of PAni/DBSA (bottom line) and PAni/HCl (upper line).

Figure 3. Thermogravimetric analysis for different forms of PAni.
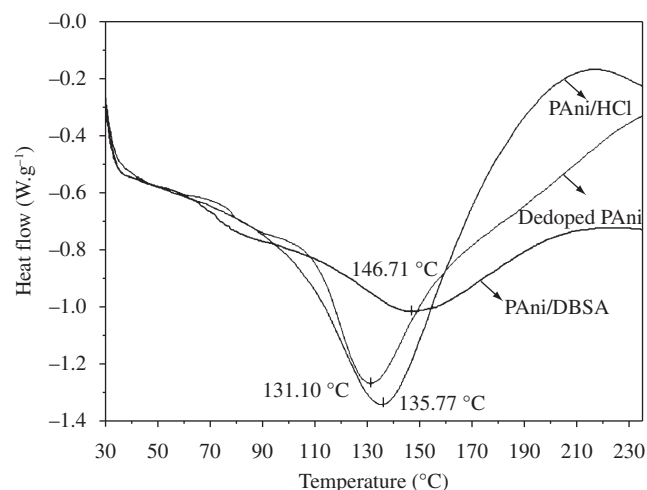
Figure 4. Differential scanning calorimetry analysis for different forms of PAni.

DSC analysis were not performed successfully in PAni's glass transition temperature (T_g point) detecting due to the usual difficulties of DSC technique, such as the lack of accuracy for determining this temperature. The Tg point of pure PAni/DBSA was reported to be around 130 °C, lower than the Tg of dedoped PAni (over 200 °C). This is the result of plasticization effect of the DBSA dopant[16].

3.2. Characterization of PAni/LDPE blends

The conductivity of PAni/LDPE blends increased gradually with the increase of PAni concentration until a stabilization level that indicates the percolation threshold of PAni in LDPE matrix (Figure 5). This percolation threshold was found around 10% of PAni/DBSA in LDPE matrix. The conductivity of blends composed by LDPE and only 1 and 5 wt. (%) of PAni/DBSA was in the order of 10^{-6} and 10^{-3} S.cm^{-1}, respectively. According to FAEZ et al.[17], a conductivity range from 10^{-11} to 10^{-2} S.cm^{-1} is considered appropriate to antistatic packaging applications. Blends of LDPE and 5 wt. (%) PAni were chosen for blends characterization by other techniques.

Figures 6a,b,c show the typical nanosized dot-like aggregates of PAni (white parts) in LDPE matrix also reported by Jianming et al.[18]. In Figure 6c it was possible to observe the fine fibrillar structrure of PAni/DBSA with a higher magnification. According to SEM experiments performed by Zilberman[19] and Leyva et al.[20], upper the percolation threshold, the PAni/DBSA structure forms an interconnected matrix through the insulator matrix, allowing the electric conductivity of the mixture in the optimum level. The level of interaction between the PAni and the matrix polymer determines the blend morphology and, thus, its electrical conductivity. Similar solubility parameters of the two polymeric components are necessary for a high level of PAni dispersion within the matrix polymer and, thus, enable the formation of conducting paths at low PAni content. According to Zilberman[19], PAni can be present in two-structure hierarchy in blends with thermoplastic polymers: a) a primary structure composed of small dispersed polyaniline particles; and b) a short-range fine fibrillar structure, interconnecting the dispersed particles. Also, these two morphologies were found in this work.

Figure 7 shows thermograms of PAni/LDPE blends. The degradation temperature was around 480 °C, the same as pure LDPE. Thus, the thermal stability of PAni/LDPE blends were the same as the LDPE. Some LDPE samples were processed once in a double-screw extruder and blended with PAni in the same conditions of the virgin LDPE. No significant change in the degradation temperature was observed by thermogravimetric analysis. DSC analyses in PAni/LDPE blend (Figure 8) showed only an endothermic peak attributed to its fusion temperature (around 120 °C). Again, no marked difference
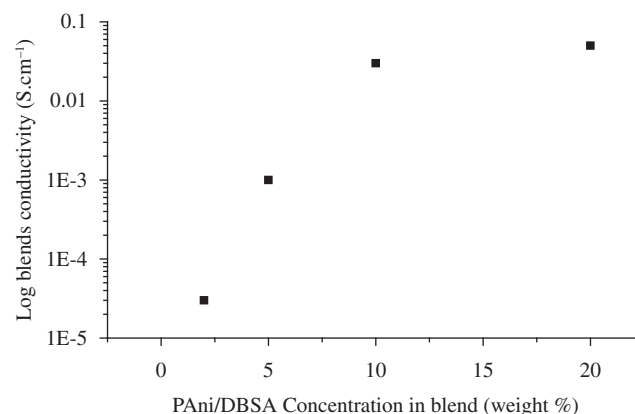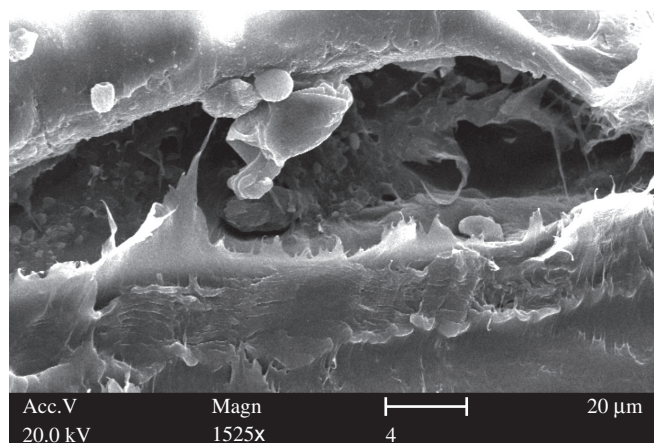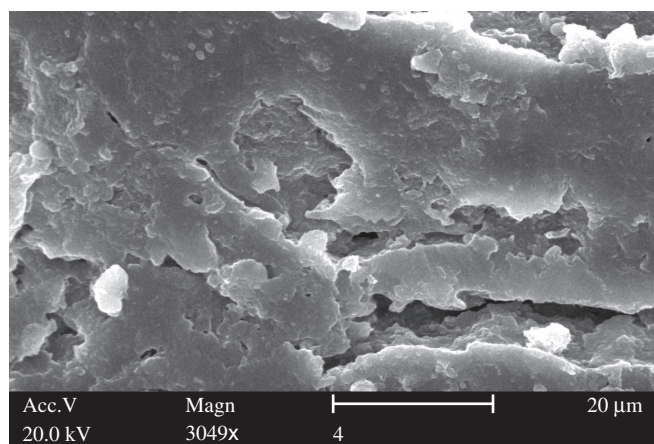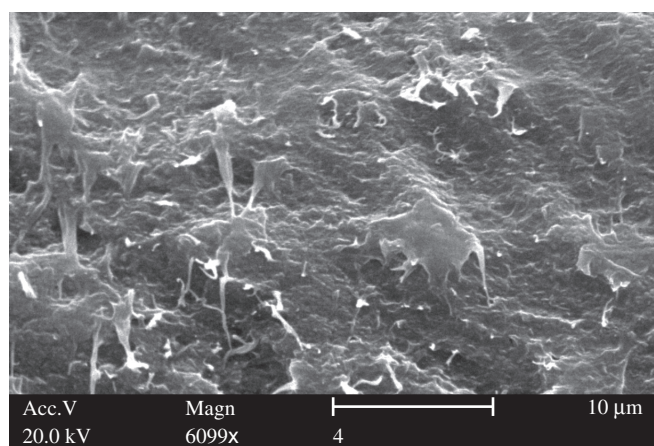

Figure 5. PAni concentration influence on PAni/LDPE blend conductivity.

(a)

Figure 7. Thermograms of PAni/LDPE blend with 5 wt. (%) PAni: continuous line – virgin LDPE and dotted line – processed LDPE.

(b)

Figure 8. DSC thermogram of PAni/LDPE blend with 5 wt. (%) PAni.

4. Conclusion

Different forms of PAni were synthesised in this work. PAni doped with dodecil benzenesulfonic acid (PAni/DBSA) showed the best combination of solubility and conductivity for blends manufacture via solvent evaporation. However, this form of PAni is less thermal stable, starting its decomposition process at around 250 °C. A blend composed by a mix of 5 wt. (%) of PAni/DBSA and LDPE showed a degradation temperature of 480 °C and a conductivity in the order of 10^{-3} S.cm^{-1}. Thus, the PAni/DBSA has a great potential to be blended with LDPE in order to be used in antistatic packaging. The use of processed LDPE in the blends manufacture presented a new opportunity to increase the aggregated value of the recycled material. The next step of the research is to investigate the thermal properties of the blend by DMTA (dynamic-mechanic-thermal analysis) technique. This information is helpful for processing PAni/LDPE blend in industrial processes like extrusion and injection moulding.

(c)

Figure 6. Scanning electron micrographs of the cross-section of PAni/LDPE blend with 5 wt. (%) PAni: a) 1500x; b) 3000x; and c) 6000x.

between PAni/LDPE blend and pure LDPE thermal behavior could be detected. Also, blend's fusion temperature was equivalent for either virgin or processed LDPE as blend matrix. The homogeneity of the blends could not be determined accurately through the use of DSC because no Tg value was detected.
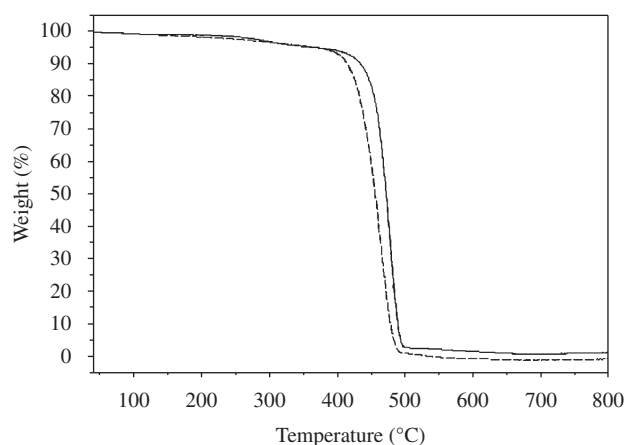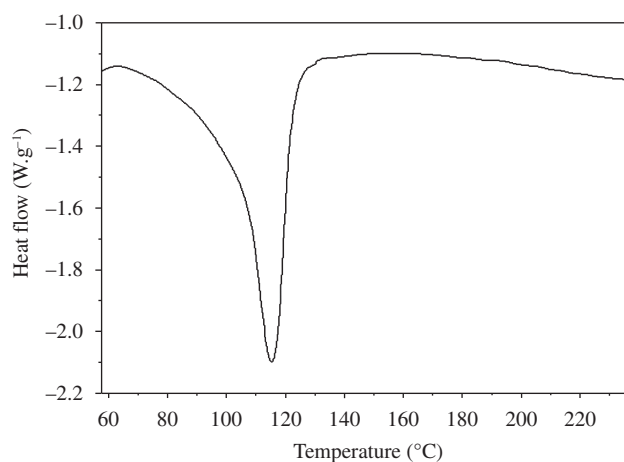
Acknowledgments

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