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Synthesis and Characterization of Conducting Composites of Polyaniline and Carbon Black with High Thermal Stability

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Abstract: In this work, a detailed chemical route to prepare thermally stable polyaniline (PANI)/carbon black (CB) composites is described. The syntheses were performed by chemical polymerization of aniline over CB particles, using different PANI/CB mass ratios. The thermal and electrical properties were characterized. Composites with mass ratio up to 65:35 (PANI:CB) showed excellent thermal stability maintaining their conducting properties when thermally treated at 230 °C for two hours, which is adequate to process these materials. Moreover, the results showed an important reduction in the surface area of the composites which have a good relationship with the improvement of the rheological properties in melt processing.

Keywords: *Composite materials, electrical properties, conducting polymers, thermal properties.*

Introduction

PANI presents very poor mechanical stability in its conducting state, which requires the preparation of copolymers or blends. Moreover, the polymer must be stable at the high temperatures that are necessary for processing[1-16]. However, films prepared with intrinsically conducting polymers (ICPs) exhibit poor mechanical properties and are also thermally unstable[17,18], for example, conducting PANI loses its electrical properties at 225 °C, even under nitrogen atmosphere.

Generally, thermoplastics or thermosets conductive compounds are obtained by the addition of a conductive loading, such as CB, to the polymeric matrix. Additionally, to obtain suitable materials, high loadings of the additive are necessary. This makes heat processing difficult, because the high surface area additive increases the melt viscosity in the interaction with the polymer matrix[19,20].

Composites obtained by deposition of ICPs over CB particles, showed thermal stability and effective reduction of the surface area and pore volume of the CB[18,21]. These classes of composites could be obtained by the *in situ* deposition of the ICP on CB substrate[18,22], the direct polymerization of ICPs on carbon substrates, by chemical[23,21,24] or electrochemical method[25-28]. The chemical process yields to large quantities of ICPs[29].

These ICPs/CB composites are generally applied in static dissipative compounds[19,20]. In addition, composites based on ICPs over carbon substrates, such as graphite and carbon nanotubes, have been investigated aiming at different applications, such as, electrochemical sensors of pesticides[23], charge storage devices[24,25,30], electrocatalytic methanol oxidation[27] and sensors to detect and discriminate biogenic amines[31]. Specifically, PANI onto carbon nanotubes substrates have demonstrated some properties such as the increase of the PANI conducting ability[27,32,33], the supercapacitive behavior[30,34] as well as better recovering properties by functionalizing the oxidized carbon nanotube with p-phenylenediamineamino before starting the polymerization[35]. Nevertheless, the attainment of a well controlled carbon nanotube substrate, with high purity degree, is still difficult and expensive.

In this work, a detailed and simple route is described to prepare composites based on the direct chemical polymerization of PANI onto particles of conductive CB substrate (type Printex® L6 from Degussa S.A). It is also demonstrated that this procedure presents great advantages such as the best control in the substrate recovering. The composites were characterized by thermal analysis, specific area, elemental analysis and AC conductivity.

Experimental

Aniline (Aldrich) was purified by distillation under reduced pressure in the presence of zinc powder. Conductive CB Printex® L6 (10^{-1} S cm^{-1} in pressed samples) was purchased from Degussa. All reagents were analytical grade and used as received. The water used for the solutions was purified by the Milli-Q system (Millipore Inc.).

The PANI was synthesized using aqueous HCl by the direct oxidation of the aniline with the addition of a solution of 0.25 M $(NH_4)_2S_2O_8$ using a monomer:oxidant molar ratio of 4:1 at 0 °C. The resulting PANI powder was dried under air atmosphere at 60 °C.

The composites were prepared by maintaining CB under mechanical stirring for 1 hour in contact with acidic aqueous solutions of 1.0 M aniline in 1.0 M HCl. After that, the solution of 0.25 M $(NH_4)_2S_2O_8$ in 1.0 M HCl was drop wise

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added to the monomer solution and the reaction occurred for 2 hours.

After the chemical polymerization, the resulting powder was washed with 1.0 M HCl solution and dried at 60 °C for 24 hours. Composites were prepared with different mass quantities of CB, namely, 10, 20, 35, 50 and 63 mass %, considering a yield of 50% of the PANI chemical polymerization.

The real amount of PANI in the composites was measured by the elemental analysis (C, H, N e S) using a Fison analyzer model EA 1108. The compositions were calculated quantifying the nitrogen atoms that correspond to each monomeric unit of PANI in the sample.

The composites and CB specific areas were measured under nitrogen atmosphere at 200 °C for 1 hour. A BET analyzer from Micrometrics model ASAP 2000 was used.

Thermal analyses were performed under air atmosphere using a Netzch thermal analysis instrument model TASC 414 with scan rate of 10 °C/min.

Sample pellets were used for the electrical characterization. The electric contact was established at two opposing faces of the pressed samples using two platinum disc electrodes. The analyses were performed in a Solartron model 1260 frequency response analyzer, by changing the frequency from 1 MHz to 1 Hz, applying a 15 mV AC potential.

Results and Discussion

Previous studies showed that the molecular weight of PANI can be substantially increased by the oxidative polymerization of aniline with ammonium peroxydisulfate just decreasing the temperatures and also dissolving selected neutral salts. The molar ratio monomer:oxidant also gives a product with high molecular weight[36]. Moreover, the procedure of washing the polymer with acid solution removes soluble impurities such as oligomers, etc.

The real mass proportions of chemically polymerized PANI in the composites were determined using elemental analysis and compared with the nominal compositions. Table 1 presents the calculated compositions of PANI:CB, 37:63; 50:50 and 65:35, considering the sum of %C + %H + %N as 100%. Sulfur impurities were attributed to traces of ammonium persulfate and were not calculated.

The results depicted in Table 1 showed that the yielding of the chemical synthesis of the composites was comparable to the expected values.

The measurement of the specific area of an additive is very important to determine the transport properties, as well as the formation of the particles network. The decrease of the specific area improves the rheological properties, and consequently the processing of this material at high temperatures[18-20]. Figure 1 presents results for CB and different samples of the composites.

Table 1. Percent of PANI in the composites determined by elemental analysis.

Nominal content of PANI:CB	Real amounts of PANI (%) in the composites
37:63	40.9
50:50	44.2
65:35	59.9

The CB Printex® L6 from Degussa has specific area of 235 $m^2 g^{-1}$. Covering CB substrate with a PANI layer during its polymerization also produces a five-fold reduction of the specific area for the composite PANI:CB 50:50. As a comparison, in a commercial sample (KP40 from Eeonyx Co) the deposition of 40% of PANI onto CB substrate reduces the specific area about three times[18]. The decrease of the CB specific area after the *in situ* polymerization of PANI was attributed to better sorption of aniline monomer onto CB particles as compared to the commercial one.

Figure 2a presents the TGA curves for pure PANI obtained under air atmosphere. For better visualization of these results, Figure 2b presents the first derivative of the thermogram curves presented in Figure 2a.

In this figure, a mass loss is observed starting at temperatures higher than 100 °C with 65% of residue at 500 °C. The results presented in Figure 2b showed that PANI shows an intense peak between 130 and 210 °C. This peak corresponds to PANI dedopping process with the exit volatilization of both HCl and other small molecules[17,18]. An accumulated 7% mass loss was observed between 130 and 200 °C. This mass loss could be attributed to the elimination of water and HCl molecules (doping molecules) in agreement with literature data[18]. No mass loss was observed for the CB L6 (CB). For the composites, the TG curves show an intermediate behavior, which is proportional to the quantity of the CB in the sample. A stable behavior was observed for the 37:63 composite without any mass loss up to 250 °C, followed by a linear loss and with a residue mass of 93% at 500 °C. The composites PANI:CB ratios 65:35 and 50:50 of CB exhibited a thermal degradation at 100 °C, followed by a mass loss,

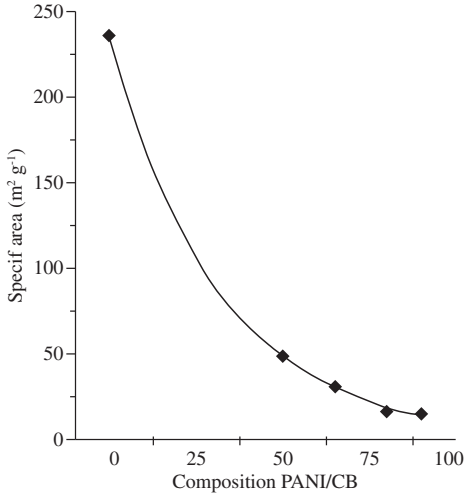
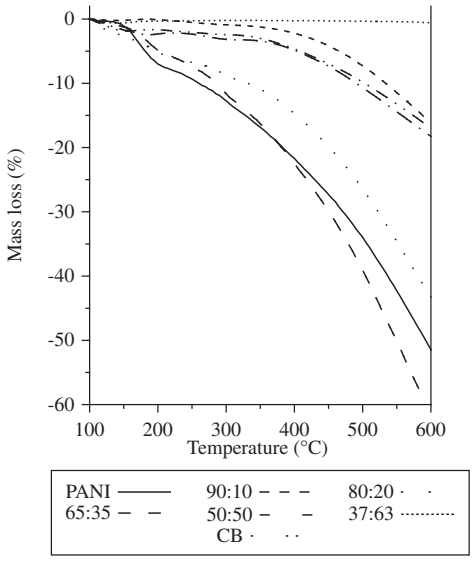
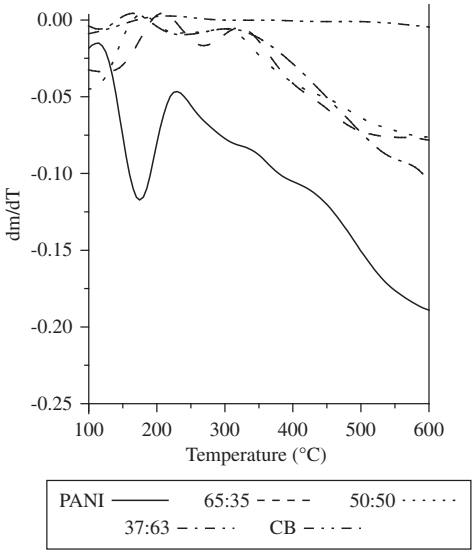


Figure 1. Specific area of the composites PANI:CB 50:50, 65:35, 80:20 and 90:10 obtained by BET analysis.



(a)



(b)

Figure 2. a) TG curves performed at a scan rate of 10 °C/min in air; and b) Differential TG curves.

leading to 90% of residue at 500 °C. The 80:20 and 90:10 composites are more unstable with mass loss of 5% at approximately 200 °C, which was attributed to the loss of water and HCl. These results are in agreement with the explanation that the CB substrate acts as a barrier preventing the elimination of small molecules at elevated temperatures[1,18].

In order to study the changes in the electrical properties, sample pellets of the composites were thermally treated for two hours at different temperatures under air atmosphere before each measurement. Figure 3 shows the results of the log of the Electrical resistance (in Ω) as a function of the temperature (°C) to the obtained composites.

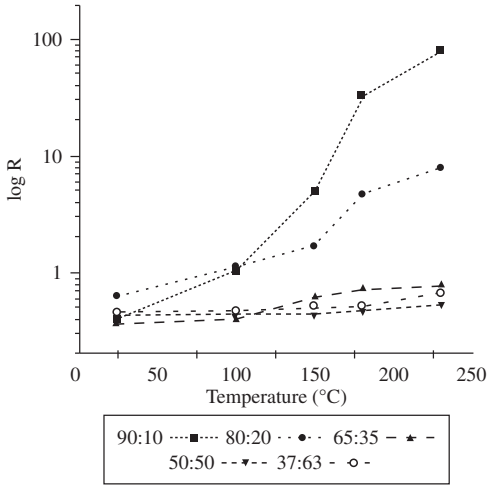


Figure 3. Electrical resistance (in Ω) as a function of temperature of the composites PANI:CB.

No significant variation of the electrical resistance was observed for the compositions up to PANI:CB 50:50. From the composition PANI:CB 65/35 onward, the samples show loss of conductivity which is evidenced by the increase of the electrical resistance. However, even after thermal treatment, all the analyzed composites showed values of electrical resistance lower than 100 Ω, which represents some conductivity remaining in the material.

Conclusions

A simple method to prepare PANI:CB composites by the direct chemical polymerization of aniline in the presence of a CB dispersion under stirring was described. The nominal contents of PANI in the composites (considering a yielding of the synthesis of 50%) were very similar to the ones determined by elemental analysis. The BET analysis showed that the composites had about five-fold surface area reduction to compositions of 50% of PANI. This condition can improve the rheological properties during the heat processing. It was also observed, by thermal and a.c impedance analysis, that the composites presented high thermal stability without degradation of the electrical characteristics for compositions up to PANI:CB 65:35. We suggest these materials to be used in future studies as antistatic additives with melt processing and other applications such as sensors and charge storage devices.

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