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Physical and conductive properties of the blend of polyaniline/dodecylbenzenesulphonic acid with PSS

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Summary

Polyaniline, PAni, has very promising industrial applications because of its good environmental stability, low cost and simple synthesis. Polyaniline doped with organic protonic and polymeric acids shows improved solubility and processability by conventional methods. In this work we report the results of doping polyaniline with dodecylbenzenesulphonic acid (PAni-DBSA) and reprocessing with polystyrene sulphonic acid (PSS) in an internal mixer, to obtain a conductive polymer blend (PAni-DBSA/PSS). This investigation of the blend properties focused on the thermal stability, calorimetric behaviour and resulting electrical conductivity.

Introduction

Polyaniline excites special interest, within the field of conducting polymers, for a number of important reasons [1] monomer (aniline) cost, a wide range of applications, simple polymerization methods and a polymerization reaction with high yield. Furthermore, its electrical properties can be reversibly controlled both by charge-transfer doping and by protonation. Its wide range of associated electrical, electrochemical and optical properties [2], coupled with good stability, make polyaniline potentially attractive for application as an electronic material, for antistatic coatings, anticorrosive protection, etc [3].

Processing of polyaniline has remained a difficult problem; polyaniline cannot be processed by the methods routinely used in the plastic industry. Melt processing of PAni is not possible because it begins to degrade at temperatures below its softening or melting point [4]. Besides, pure polyaniline has poor mechanical properties. However, some methods have been reported directed towards improvement of the processability of polyaniline-based conducting polymers. Redoping of PAni with functionalized organic acids, such as dodecylbenzenesulphonic (DBSA) [5], p-toluenesulphonic [6] and camphorsulphonic acids [7], both by solution casting from nonpolar or moderately polar organic solvents [5] and by melt processing [8], results in doped PAni with improved thermal stability and processability.

Polyaniline has also been doped with a polymeric acid [9] showing improved solubility and processability. As described by Fu and Weiss [10], lightly sulphonated polystyrene (HSPS) was chosen as the polymer matrix because the randomly placed sulphonic acid groups on the polystyrene chains behave as a dilute acid. The acid will protonate the imine nitrogen sites of polyaniline, while possibly retaining the processability of polystyrene. In addition, they studied the doping of PAni through protonation by sulphonic acid groups of HSPS (5.3 mol %) in solution and its dependence on the solvent environment. This molecular protonation should promote compatibility between polyaniline and polystyrene within the blends and simultaneously transform the insulating polyaniline base form to the metallic conducting form, thereby rendering the blends conductive. The use of polymeric dopants may significantly improve the stability of the resulting polymers blends, because small molecule dopants tend to migrate out of the polymer matrix.

Additionally, in another doping approach [11], the PAni(DBSA) complex was prepared in the absence of solvents by heating at an elevated temperature, resulting in "thermal doping". In addition to doping polyaniline, this method introduces substituents to its backbone without using auxiliary solvents. The presence of excess DBSA, only physically mixed with PAni, leads to a dispersion of PAni particles in DBSA, forming a paste. Heating causes solidification of the paste, and PAni(DBSA) becomes electrically conducting (typically 1 to 10 S cm^{-1}). Recently, thermo-mechanical methods were used for PAni processing without auxiliary solvents or polymers. Moreover, doping was carried out during processing, eliminating several processing steps. We have called this "reactive processing" [12].

The objective of the present study is to investigate the doping of PAni(DBSA) with a third reactive component, polystyrene sulphonic acid (PSS) and to evaluate the associated protonation reaction product. The main advantage of this new blend is the possibility of producing conductive polyaniline blends with PS thermoplasticity, where PSS can be used as compatibilizer in the PS matrix.

Experimental

Poly (styrene sulphonic acid) synthesis

Polystyrene (Piramidal Termoplásticos, São Bernardo do Campo, M_w = 166 000) was sulphonated in CH_2Cl_2 at 40 °C with acetyl sulfate according to our patented procedure [13]. This new procedure is similar to the sulphonated polystyrene prepared using the procedure patented by Makowski et al. [14]; the difference resides in the solubilization step of the amorphous thermoplastic using a different solvent. In our method the synthesis was done on a pilot plant scale, using less harsh conditions and thus lowering energy consumption.

The sulphonation level was determined by titration of the PSS solution in methanol to a phenolphthalein end point, using sodium hydroxide in methanol as titration agent. In this work the sulphonation levels achieved and used were 18 and 20.1 mol % (PSS_2 and PSS_4, respectively). The PSS was stored in a desiccator with $CaCl_2$, due to its extremely hygroscopic nature.

Reactive processing

PAni(HCl) was prepared according to a previously published route [15] and dedoped in a 1 mol L^{-1} NH_4OH aqueous solution under stirring for 24 h, precipitated, filtered, rinsed with water and alcohol, and dried at 90 °C. The resulting emeraldine base polyaniline (PAni EB) was doped with different concentrations of dodecylbenzenesulphonic acid (DBSA), resulting in PAni(DBSA)$_y$, where y is the molar ratio of DBSA, corresponding to 0.25 and 0.5, respectively (for these ratios we consider that one unit of PAni has four monomeric units) [16]. PAni EB and DBSA were mixed at room temperature resulting in a powder. Immediately thereafter the conductive polymer was prepared by processing in a double screw counter rotatory internal mixer coupled to a Haake Rheocord 90 rheometer [17]. Mixing time was 20 min at 150 °C and 25 rpm. Afterwards, PAni-DBSA was cooled, removed from the mixer, ground and reprocessed with the third reactive component, the polystyrene sulphonic acid (PSS), under the same processing conditions (25 rpm, 20 min and 150 °C), using PSS with different degrees of sulphonation. The formulations of the blends are indicated in Table 1.

Characterization

Thermal stability of the blends and the pure components was studied by thermogravimetry (TGA) in a DuPont 951 thermal analyzer, from 25 °C to 900 °C (heating rate of 10 °C min^{-1}) under an argon atmosphere. For the pure samples the analysis upper temperature was 500 °C. All samples were previously heated to 100 °C for 5 min to eliminate residual water (humidity). Differential Scanning Calorimetric (DSC) measurements were performed in a TA Instruments 2100 analyzer from 30 to 300 °C at 20°C min^{-1}, under N_2. All samples were submitted to a first heating (30 to 300 °C) followed by an isotherm for 5 min at 300 °C, cooling to 30 °C, isotherm for 5 min at 30 °C and a second heating cycle (30 to 300 °C), to evaluate the irreversible transitions. The curves reported correspond to the second heating. Infrared spectra were recorded using a Perkin-Elmer FT-IR 1600 spectrophotometer. PSS samples were measured in KBr and the PAni complexes as Nujol emulsions. Conductivity measurements were carried out on flat plaques (6.5 x 6.5 x 0.2 cm) prepared by compression molding at 150 °C and 4.5 MPa of pressure during 20 min and measured by a Cascade Microtech C4s-64 four probe system coupled to a Keithley 617 electrometer and a ET-2500 multimeter [18,19].

Results and Discussion

The doping of PAni EB with DBSA and the blending processing with PSS were carried out in a counter rotatory double screw internal mixer. Torque and temperature changes were monitored as a function of mixing time (figure 1). Following charging of the mixing head, preheated to the desired temperature (150 °C), with the premixed samples (in the form of a paste), the temperature increased during the processing by several degrees. Thus, the thermal doping reaction is accompanied by heat generation (due to shearing of the thermoplastics by the rotors) and yields doped PAni-DBSA$_y$. Similar heating is observed upon addition of polystyrene sulphonic acid to the mixture. The PAni-DBSA$_y$-PSS$_x$ blend has a highly viscous consistency, resulting in a marked torque increase.

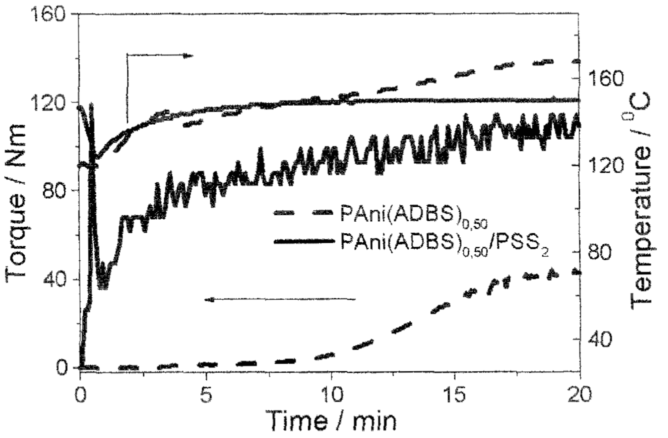

Figure 1. Torque and temperature curves as a function of processing time for PAni(DBSA)$_{0.5}$ and PAni(DBSA)$_{0.5}$/PSS$_2$

The doping reaction is shown in figure 2. We propose the hypothesis that the reaction preferably occurs on the protonated imine sites of polyaniline.

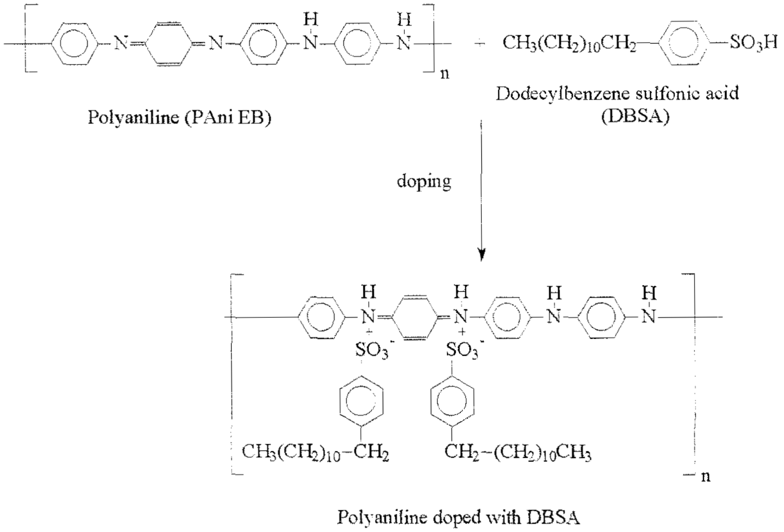

Figure 2. Mechanism of PAni doping with DBSA.

Thermogravimetric analysis of pure PAni EB, DBSA and the doped PAni-DBSA are presented in figures 3a and 3b. These curves compare the thermal stability of the samples under an inert atmosphere. DBSA shows one sharp weight loss process starting at 160 °C, leading to a 75 % weight reduction [20]. PAni EB, on the other hand, shows a smooth weight loss curve with onset at approximately 400 °C. The doped polymers show intermediate behaviour, with two weight loss processes. The first weight loss resembles that of DBSA, with a slight increase in the onset temperature, probably caused by the low thermal diffusion coefficient of the polymer or by the chemical changes induced by the doping reaction. The second process resembles that of PAni EB. However, for the polymer with a higher dopant concentration (figure 3b), there is a third intermediate change.

In order to identify which processes are occurring in the complexes, we simulated the thermogravimetric curve for the conductive complex by averaging the curves of its pure components and assuming that there are physical and also chemical interactions between the acid and the polymer dopant during processing [21]. The shift of the experimental curve in relation to the calculated curve for the doped polymer confirms the doping reactions.

Figures 4a and 4b compare the thermogravimetric curves for the blends and its components. The kinetics of degradation is modified with the presence of PSS, showing a fast degradation of the polymer. The effect caused by interaction between the components of the conductive complex is evident when we observe a comparison of the calculated curve and the thermogravimetric curve for the conductive complex (figures 4a and 4b).

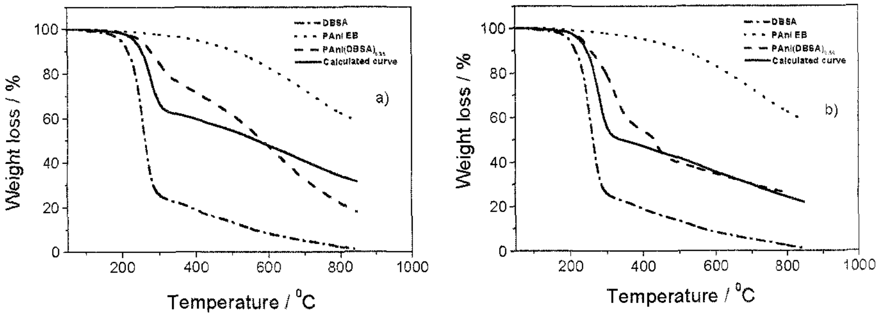

Figure 3. TGA curves measured under Ar and heating rate of 10 °C min^{-1} for: a) PAni(DBSA)$_{0.25}$ and its components and b) PAni(DBSA)$_{0.5}$ and its components

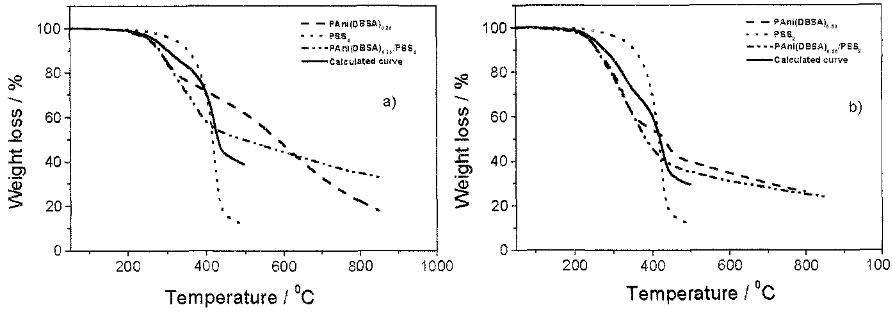

Figure 4. TGA curves measured under Ar and heating rate of 10 °C min^{-1} for: a) PAni(DBSA)$_{0.25}$ / PSS$_4$ and its components and b) PAni(DBSA)$_{0.5}$ / PSS$_2$ and its components

The protonation reaction of PAni with these acids can be also observed in the DSC curves of figures 5 and 6. From the literature [8], the PAni-DBSA complex exhibits an exothermic peak at ca. 150 °C, where the pastelike consistency transforms into a solidlike material, but the temperature depends on the PAni-DBSA ratio. A defined exothermic peak at an elevated temperature, where the conducting complexes PAni(DBSA)$_y$ and PAni(DBSA)$_y$PSS$_x$ are formed, is observed in the first heating, figures 5a and 5b. These transitions are irreversible, as is shown in figures 6a and 6b during the second heating. Both samples of PSS present an endothermic peak at 200 °C, which could be assigned to sulphonated groups present in the polymer chains. They cannot be assigned to crystalline melting because X-Ray diffraction analysis indicates that both PSS are amorphous. This behaviour also cannot be assigned to the pure PS melting point, because PS is also amorphous. In contrast, the glass transition temperatures of PSS are shifted to higher temperatures, as compared to pure PS (from 100 to 130 °C). No transitions were observed in the second heating of the DSC analyses for PAni EB, PAni(DBSA) and PAni(DBSA)/PSS. This is an indication of the doping reaction by PSS (figures 6a and 6b).

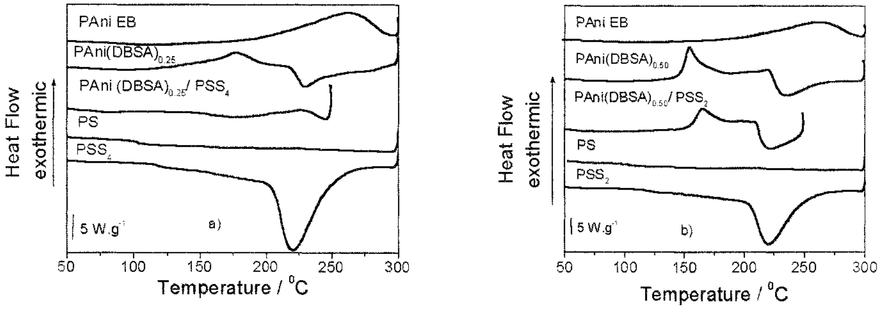

Figure 5. a) DSC curves for PAni EB, PAni(DBSA)$_{0.25}$/ PSS$_4$ and its components and b) DSC curves for PAni EB, PAni(DBSA)$_{0.5}$/ PSS$_2$ and its components. Both are first heating

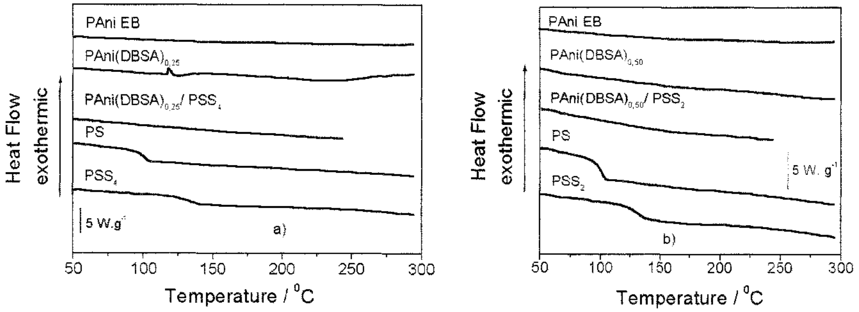

Figure 6. a) DSC curves for PAni EB, PAni(DBSA)$_{0.25}$/ PSS$_4$ and its components and b) DSC curves for PAni EB, PAni(DBSA)$_{0.5}$/ PSS$_2$ and its components. Both are second heating

By comparing the FT-IR spectra of pure PS and PSS we observe that the absorptions at 1040 cm^{-1} and 1180 cm^{-1} confirm the presence of SO_3H groups. In the spectra of polyaniline emeraldine base, PAni(DBSA)/PSS and PAni(DBSA), we observe an absorption at 1200 cm^{-1} characteristic for out-of-plane and in-plane bending of C-H bonds of aromatic rings present in PAni. Also, the spectrum of Pani(DBSA)/PSS, corresponds to a superposition of the spectra of the components of the blend.

The blend formulations and electrical conductivities of samples are presented in Table 1. Apparently, all the doped complexes PAni(DBSA)$_y$ and PAni(DBSA)$_y$PSS$_x$ are conductive when we compare with the emeraldine base (for PAni EB or pure PS, $\sigma < 10^{-12}$ S cm^{-1}). The variation of conductivity for different dopant concentrations produced the expected effect. The complex PAni(DBSA)$_{0.50}$ is more conductive than complex PAni(DBSA)$_{0.25}$ due to the complete reaction of protonation. In this case we suggest that all imine sites of the emeraldine base polyaniline react with DBSA, resulting in the protonated PAni(DBSA)$_{0.50}$ complex.

Table 1. Blend formulations used in this work and their conductivities measured by the four probe method.

Samples	PAni EB (g)	ADBS (g)	PSS (g)	Four probe method (σ, S cm^{-1})
PAni(DBSA)$_{0.25}$	26	24	–	$(1.81 \pm 0.02) \times 10^{-2}$
PAni(DBSA)$_{0.5}$	18	32	–	$(4.32 \pm 0.08) \times 10^{-2}$
PAni(DBSA)$_{0.25}$/PSS$_4$	28		22	$(1.56 \pm 1.10) \times 10^{-4}$
PAni(DBSA)$_{0.5}$/PSS$_2$	32		18	$(2.98 \pm 0.01) \times 10^{-3}$

The conductivity results obtained for the complex PAni(DBSA)$_y$ are comparable to those described in the literature [12]. In spite of the different degrees of sulphonation used, we observed that the presence of PSS in the complex produced, for PAni(DBSA)$_{0.50}$/PSS$_2$, an increase in conductivity of ca. one order of magnitude as compared to PAni(DBSA)$_{0.25}$/PSS$_4$. This was expected because a 50 % content of DBSA in PAni produces a more conductive material than that with 25 %. This confirms that PSS cannot be used as a dopant in the PAni(DBSA)$_{0.50}$ complex. On the other hand, we suggest that PSS is playing the role of dispersing aid in the complex PAni(DBSA), improving the interactions of this complex and consequently the results of electrical conductivity.

Conclusions

Reactive processing is a convenient method to improve the processability and to dope the intrinsically conducting polymers; also it allows working in the absence of solvents. The doping process occurs during processing in the mixer. We prepared a conductive complex (PAni-DBSA/PSS) and observed that, by changing the concentration of PAni-DBSA, it was possible to improve the conductivity properties (10^{-5} to 10^{-3} S cm^{-1}). These results suggest the potential application of these complexes for electrostatics and static discharge dissipation [22], where the required conductivity levels are in the same range as our results. In forthcoming studies we will report in detail the effects of the changing concentrations of DBSA on the morphology. In this study, PSS was used as a third component and we are inclined to believe that its presence will make it possible to study blends between thermoplastics, where PSS can be used as compatibilizer.

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