Conductive Polyaniline–Polyamide 6 Blends Processed from Formic Acid with Improved Stability against Deprotonation

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ABSTRACT: Stability against deprotonation of polyaniline–polyamide 6 blends processed from formic acid can be significantly improved by the addition of a supporting protonating agent to the processing solution such as phenylphosphonic acid, camphorsulfonic acid, 2-acrylamide-2-methyl-1-propane sulfonic acid, or dibutyl phosphate. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1423–1426, 1999

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INTRODUCTION

Preparation of blends of inherently conducting polymers with industrial polymers has attracted significant research attention in the last decade. Several methods of the preparation of such blends have been proposed, for example, electropolymerization[1] or chemical polymerization[2] of a conductive polymer within the insulating polymer matrix. Such preparation methods are, of course, of limited technological use. For this reason more recently thermal[3] and solution[4] processing of polyaniline-based blends have been studied.

It has been demonstrated that doped, i.e., conductive, polyaniline can be dissolved in a variety of solvents if appropriately functionalized protonic acids are used as doping agents.[5] The physical nature of these polyaniline solutions is still the subject of a scientific debate—are they true molecular solutions or colloidal dispersions?[6] However, independent of their true physical state, they can be used in solution processing to give thin layers, free standing films, or fibers of conductive blends.

Solution processing of conductive blends is conceptually very simple. It consists of codissolution of two constituents of the blend (conductive and insulating) in a common solvent followed by evaporation of this solvent. Depending on the solidification conditions, different morphologies of the conductive phase can be obtained, which in turn, may lead to different percolation thresholds for conductivity. Successful preparation of polyaniline–poly(methyl metacrylate),[4] polyaniline–ABS,[7] polyaniline–acetate cellulose,[8] and polyaniline–poly(vinyl alcohol)[9] composites with a percolation threshold well below 1% have been reported. However, preparation of polyaniline blends by casting from solution frequently requires the use of "exotic" and expensive solvents such as, for example, hexafluoro-2-propanol[10] or solvents hardly acceptable by industry such as *m*-cresol and other phenols.

It has been known since 1988[11] that polyaniline can be processed from formic acid. Because formic acid is a good solvent for polyamide 6, blends of polyaniline with nylon can be prepared by solution processing. Such blends have recently been obtained by Abraham et al.[12] Formic acid, as

applied by these authors, plays a double role. It dissolves polyaniline and protonates it at the same time. Thus, the polymer is rendered conductive by its interaction with the solvent. The blends were, therefore, prepared in a three-component system: polyaniline–formic acid–polyamide 6, without the use of an additional protonation agent. In the conclusion part of their article the authors state that the prepared blend exhibits good environmental stability. It should, however, be mentioned that formic acid, being a rather weak acid, is not a very good protonating agent for polyaniline. One may expect that blends prepared on the basis of formic acid-doped polyaniline may have the tendency to deprotonate and gradually loose their conductivity. The main goal of this research was to verify the stability of polyaniline–formic acid–polyamide 6 blends with respect to deprotonation, and to find a way to improve this stability. Our idea was to find a more efficient protonation agent which, if added to the polyaniline–formic acid solution, would exchange with HCOOH as a polyaniline dopant at the final stage of the composite casting.

EXPERIMENTAL

Polyaniline was synthesized using a method described before.[13]

Polyaniline–polyamide 6 blends were prepared by mixing 1 wt % solutions of PANI base in 80 wt % formic acid with 2 wt % solutions of polyamide 6 in 80 wt % formic acid in different ratios to give, after casting, blends with the PANI content from 1 to 50 wt % . Two types of blends were prepared: (1) without the additional protonating agent as in ref. 12; (2) with supporting protonating agents that were added in the molar ratio of 0.5 acid molecule per PANI repeat unit involving one ring and one nitrogen atom, i.e., to give $PANI(HA)_{0.5}$ assuming complete protonation. It is difficult to find an appropriate protonating agent that would not cause immediate precipitation of polyaniline after its addition to PANI–formic acid solutions. We have tested several functionalized acids and acidic ester, and we found four that do not promote phase separation. These are: phenylphosphonic acid, abbreviated as PPA; camphorsulfonic acid, abbreviated as CSA; 2-acrylamide-2-methyl-1-propane sulfonic acid, abbreviated as AMPSA; dibutyl phosphate, abbreviated as DBP.

In all the above cases no precipitate was collected after centrifugation of the solution with 5000 rotations/h.
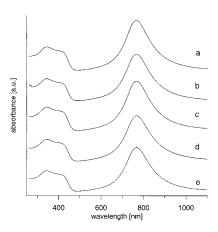

Figure 1 UV-VIS NIR spectra of polyaniline dissolved in formic acid. PANI base (a), PANI with additional protonating agents: PPA (b), CSA (c), AMPSA (d), DBP (e). The molar ratio of (acid molecule)/(PANI repeat unit PhN) = 0.5.

The spectra of formic acid solution of polyaniline as well as the spectra of films cast from these solutions were measured on a Perkin-Elmer Lambda 2 spectrometer.

Conductivities were measured using a standard four-probe method.

RESULTS AND DISCUSSION

From the UV-VIS NIR spectrum of PANI base dissolved in formic acid (Fig. 1) it is clear that the polymer undergoes protonation by the solvent. Three well-defined absorption peaks at 344, 420, and 767 nm are characteristic of protonated polyaniline with localized charge carriers (polarons).[14] The addition of a supporting protonation agent does not influence the spectra—independently of the acid admixed the spectra remain the same, essentially indistinguishable from the spectrum of PANI base dissolved in HCOOH. Because in the solution formic acid is present in a large excess with respect to the supporting protonating agent, it is highly probable that basic polyaniline sites are protonated by the solvent HCOOH molecules. This will, of course, result in identical spectra for all systems studied. Upon removal of the solvent, HCOOH molecules become gradually replaced by supporting protonating agents that are stronger acids than formic acid. Thus, for solid thin films differentiation in the spectra is expected. This is indeed the case. In Figure 2 the spectra of PANI cast from pure for-
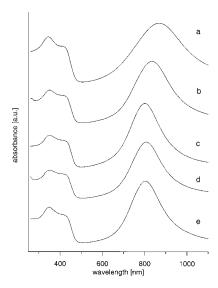
Figure 2 UV-VIS NIR spectra of polyaniline films cast from formic acid solutions of PANI base (a), PANI with additional protonating agents: PPA (b), CSA (c), AMPSA (d), DBP (e). The molar ratio of (acid molecule)/(PANI repeat unit PhN) = 0.5.

mic acid and formic acid containing supporting protonating agents are compared.

The positions of the two higher energetic peaks at 350 and 430 nm do not depend on the presence of the supporting protonating acid in the casting solutions. However, the position of the third peak varies with the composition of the solution used for casting. First, for PANI obtained from pure HCOOH, the maximum is red shifted by 104 nm with respect to the corresponding maximum in the solution spectra. Such a shift usually indicates some deprotonation occurring during the casting. Thus, for PANI cast from pure HCOOH, the degree of protonation is smaller in the solid state than in the solution. Similarly the spectra of the films obtained from formic acid solution containing PPA as the admixture show a bathochromic shift (by 65 nm) with respect to the solution spectra. The smallest shifts are observed for CSA, AMPSA, and DBP admixtures.

Blends of polyaniline with nylon processed from the three component system: PANI–HCOOH–polyamide 6 are not stable at ambient laboratory conditions, which is in contradiction with the statement given in ref. 12. In Figure 3 UV-VIS NIR spectra of PANI–polyamide (1 wt % of PANI) are collected for increasing exposure time to laboratory atmosphere. It is clear that HCOOH-doped polyaniline in the nylon matrix undergoes slow deprotonation, which is mani-
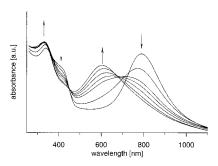

Figure 3 UV-VIS NIR spectra of PANI–polyamide 6 films collected for increasing exposure time to laboratory atmosphere. The first measurement was performed immediately after casting the film, then in 1, 2, 3, 5, 7, and 9 days.

fested by a gradual decrease of the low energetic peak intensity with simultaneous increase of the peak at 630 nm, which is characteristic of nonprotonated PANI.

The application of the supporting protonation agent, i.e., processing from a four-component system: PANI–HCOOH–supporting protonating agent–polyamide 6, efficiently improves the environmental stability of the blend with respect to the deprotonation processes. Blends containing the supporting protonating agent, when exposed to laboratory atmosphere, changed neither their spectra nor conductivity after the same period of time, which caused complete deprotonation of the blends processed from the three-component system.

The conductivity vs. PANI(HA)$_{0.5}$ content in PANI–polyamide 6 blends is shown in Figure 4 for all supporting protonating agents used in this research: (HA = PPA, CSA, AMPSA, DBP). In all cases a rather low percolation threshold is ob-
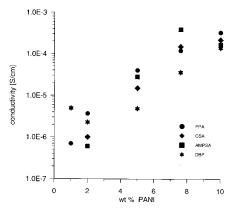

Figure 4 Conductivity vs. PANI(HA)$_{0.5}$ content in PANI–polyamide 6 blends for different protonating agents HA: PPA, CSA, AMPSA, DBP.

served. The samples down to 1 wt % of $PANI(HA)_{0.5}$ show the conductivities higher than 10^{-6} S/cm, which is above the lowest limit established for antistatic applications.

CONCLUSIONS

To summarize, we have shown that the stability of PANI–polyamide 6 blends processed from formic acid can be significantly improved if supporting protonating agents of the type of phosphonic acid, sulfonic acid, or phosphoric acid ester are added to the processing solutions. Otherwise, the conductivity of the blend gradually decreases due to the deprotonation of PANI.

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