

Preparation of Conductive Polyaniline/Nylon-6 Composite Films by Polymerization of Aniline in Nylon-6 Matrix

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ABSTRACT: Polyaniline (PANI)/Nylon-6 composite films were prepared by oxidative polymerization of aniline (ANI) inside host Nylon-6 film. Such a composite has the desired electro-active and mechanical properties to serve as a self-standing functional unit. Comparative studies on sorption of ANI by Nylon-6 matrix from various ANI containing media were conducted revealing superior ANI uptake from neutral ANI solution in water. ANI content was measured to be as high as 12%. Spectroscopic measurements showed that hydrogen bonding seemed to play important role in ANI sorption by Nylon-6 matrix. Polymerization was monitored using atomic force microscopy

and conductivity measurements. The morphology studies showed the appearance of PANI nanodomains on Nylon-6 surface in the early stages of the polymerization. Eventually the domains coalesced during polymerization forming a continuous PANI layer. The conductivity measurements confirmed the change of the morphology from isolated islands to continuous conducting surface by drastic increase in conductivity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1643–1647, 2009

Key words: composites; conducting polymers; host-guest systems; morphology; nylon-6

INTRODUCTION

Polyaniline (PANI) has been intensively studied in past decades because of potential applications in sensors,^{1–4} antistatic^{5,6} and anticorrosion^{7,8} coatings, conductive textiles,^{9–11} light emitting diodes,^{12–14} polymeric batteries, and accumulators.¹⁵ In many cases easy processability is needed for proper usage of the polymer. However, infusibility and insolubility in most of organic solvents makes PANI processing a big challenge. Extensive amount of effort has been done to overcome intractability of PANI: doping with organic acids such as dodecylbenzenesulfonic acid or camphorsulfonic acid,^{16,17} incorporation of substituents into PANI backbone such as sulfo group or carboxylic group,^{18,19} preparation of interpolymer complexes with polyanions such as polyacrylate or polystyrene sulfonate^{20,21} and making composite materials with thermoplastic polymers.^{22,23} First three methods are dedicated to enhance solubility of PANI and thus to improve solution processability. The last approach has probably greater importance because electroconductivity of PANI in composite materials is combined with good mechanical properties of thermoplastic polymer

allowing thermal processing. Also, composition of the composite can be tuned to rich optimal properties for desired application.

Composites of PANI with thermoplastic polymers can be prepared by solution casting, spin coating, electrospinning, and spraying. In all this techniques, PANI is first dissolved in an appropriate solvent together with thermoplastic polymer and then they are codeposited using one of the aforementioned methods. The result is more or less thin composite film; thickness depends on concentration of the polymers as well as on amount of solution applied. So, these techniques are restricted to film preparation and cannot be used for production of bulk composites. Another disadvantage is that PANI has to be in soluble form. It makes the process more laborious and also requires additional chemical reagents to dissolve PANI. It is another factor affecting on mixing of the polymers and thus on properties of the final composite material.

Template polymerization of aniline (ANI) inside host polymers was proposed to avoid discussed drawbacks.^{22,24–30} In early work, Chen and Fang performed electrochemical polymerization of ANI inside poly(vinyl alcohol) (PVA).²⁴ PVA layer was deposited on platinum electrode by solution casting. The electrode was then immersed in ANI monomer aqueous solution. By applying electrical potential of 1.1 V ANI from solution migrated into PVA film where polymerization occurred. PANI was first

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formed on Pt-PVA interface and then the polymerization front was moving towards PVA-solution interface thus creating gradient of PANI concentration across PVA film. More fundamental studies were done by Byun and Im.^{25–28} Nylon-6 was chosen as thermoplastic host polymer. Nylon-6 selection was justified not only by good mechanical properties but also by excellent affinity of ANI and PANI to the polymer. Indeed, amino and imino groups of PANI form hydrogen bonds with amide bonds of Nylon-6 leading to improved interaction and better ANI sorption. Nylon-6 films were soaked in pure ANI monomer and then were immersed in acidic ammonium persulfate solution for polymerization. Conductivity, transmittance, and mechanical properties of these composite films were affected by the preparation conditions.²⁵ Thermal stability studies of PANI/Nylon-6 films were performed and conductivity of the films doped with organic acids was found to be more stable than with inorganic acids.²⁶ Moreover, Neoh et al. showed that the use of sulfosalicylic acid yields composite films in which PANI is stable to deprotonation in extended exposure to water while in case of hydrochloric acid Cl^- counterions are easily removed.²⁹ Hydrogen bonding between PANI and Nylon-6 was identified by FTIR and UV-vis spectroscopy and possibly resulted in the weakening of the doping ability of PANI.²⁸

In the present work emphasis was made on investigation of ANI sorption from various ANI containing media by Nylon-6 matrix. Morphological changes during polymerization process were monitored by atomic force microscopy (AFM) and the percolation threshold in relation to conductivity was observed. Conducting properties of the PANI/Nylon-6 composite films were also studied as a function of pH.

EXPERIMENTAL

ANI, purchased from ICN Biomedicals (USA), was distilled twice before use. Nylon-6 films, obtained from Kaprolit (Russia) were 70 μm thick with 30% degree of crystallinity. ANI hydrochloride and ammonium persulfate, purchased from ICN Biomedical (USA), were used as received. Standard buffer solutions were purchased from Aldrich.

Nylon-6 films were immersed for several hours in methanol and dried in air until constant mass was observed. Films were then placed in 100 ml of aqueous ANI solution ($[\text{ANI}] = 0.38 \text{ M}$) for 10 hours. After saturation, the films were washed several times with distilled water and placed in 100 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution in 0.1 M HCl. After defined periods of time films were taken out, washed with distilled water and dried under vacuum until constant mass. In a typical procedure, $4.0 \times 10^{-3} \text{ M}$

solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 0.1 M HCl was used and the temperature of the polymerization mixture was 20°C.

To study effect of pH on conductivity of PANI/Nylon-6 composite films they were immersed in standard buffer solutions for 24 hours. After that films were rinsed with distilled water and kept at 80% humidity for another 24 hours.

UV-spectra of the PANI/Nylon-6 composite films were recorded with Specord M-40 Spectrophotometer (Germany). AFM experiments were performed using Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA) with tapping mode. Impedance measurements were performed using IPU-p.62 Impedance Analyzer (Russia) at 10–2000000 Hz frequency range.

RESULTS AND DISCUSSION

Nylon-6 films were first saturated with ANI in different media. The mass uptake was monitored as function of time for water solution of ANI (0.38 M), for aniline hydrochloride (0.38 M), for pure ANI and for water alone. Figure 1 shows that mass uptake increases linearly in all studied media during the first 2–3 hours. In the exception to the film immersed in pure ANI, all others are saturated after 4 hours and no significant mass change was further observed concluding that 2–3 hours is sufficient to reach the sorption–desorption equilibrium.

The highest mass uptake is observed for ANI solution in water, the lowest for pure ANI monomer. The latter indicates that ANI intermolecular interactions prevent the sorption process. The films have nearly twice higher mass uptake after saturation in aqueous ANI solution compared to the films after saturation in aniline hydrochloride solution of the

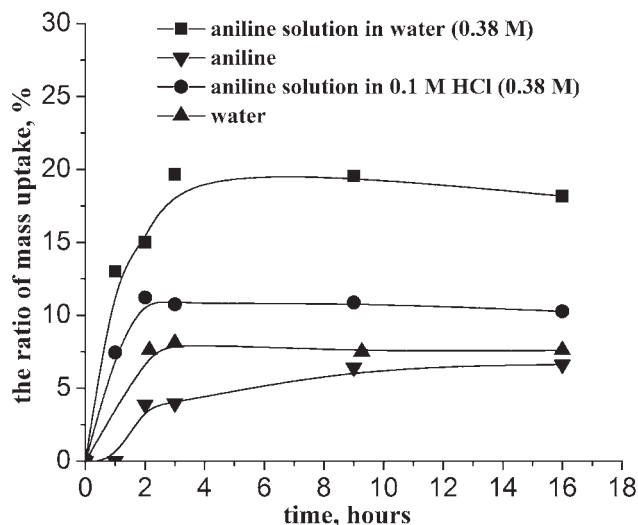


Figure 1 Sorption kinetics of aniline by Nylon-6 film.

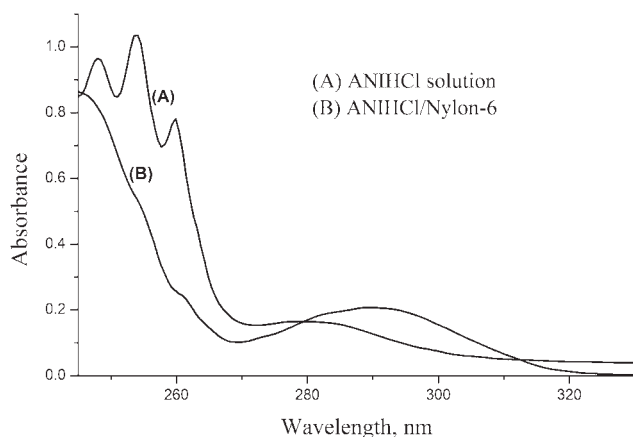


Figure 2 UV-spectra of (A) aniline hydrochloride solution (0.38 M) and (B) Nylon-6 film after saturation in aniline hydrochloride solution (0.38 M).

same concentration. It seems that also acidity of the medium plays an important role in ANI sorption into Nylon-6 matrix.

The sorption from aqueous solution of aniline hydrochloride was further investigated with UV spectroscopy to reveal the importance of interactions. UV-spectra of aniline hydrochloride solution (0.38 M) and Nylon-6 film after saturation in this solution are shown in Figure 2. ANI has absorbance maximum at 280 nm and strong broad absorbance at 230 nm, anilinium-cation has several characteristic maximums: 250, 255, and 260 nm.³¹ Maximum absorbance at 290 nm on the UV-spectrum of Nylon-6 film is attributed to ANI base form. The 10 nm red shift from 280 to 290 nm is explained by hydrogen bonding between ANI and Nylon-6 matrix.²⁸ The UV-spectrum of aniline hydrochloride solution reveal absorbance maxima at 250, 255, and 260 nm, all are characteristic for anilinium-cation.

Hereby it can be concluded only noncharged ANI molecules can be absorbed by Nylon-6 matrix. In strong acidic medium $-\text{NH}-$ groups of peptide bonds in Nylon-6 structure are also partly protonated, and the adsorption of anilinium-cations can be affected by the electrostatic repulsions between anilinium-cations and positively charged Nylon-6 surface. Other reason can be formation of stronger hydrogen bonds by $-\text{NH}_2$ groups of ANI in comparison with $-\text{NH}_3^+$ groups. Thus we selected to proceed with the effective use of aqueous ANI solution for the Nylon-6 films saturation and the further polymerization.

After the saturation in aqueous ANI solution the Nylon-6 film contains both water and ANI. To find out the amount of the adsorbed ANI, the film was immersed in water for 24 hours to extract ANI from the matrix and measure its concentration from the solution. UV-spectra of the film after the procedure showed zero absorbance at 290 nm to confirm that

ANI has desorbed completely from the Nylon-6 matrix. Extinction coefficient of ANI at 280 nm is 1400 L/mole-cm, which makes the calculation of the ANI concentration possible. 10 films were taken for statistical analysis and mass uptake due to ANI was measured to be $12.7\% \pm 0.5\%$ ($\sigma = 0.95$), while the total mass uptake (ANI and water) is $17.8\% \pm 0.8\%$ ($\sigma = 0.95$).

The Nylon-6 films saturated with ANI were placed into acidic (0.1 M HCl) solution of ammonium persulfate (4.0×10^{-3} M) for the polymerization. UV-spectra taken at different time intervals during the ANI polymerization in the Nylon-6 matrices are shown in Figure 3. The films became green after 5 minutes. The absorption maximum at 821 nm characteristic for $\pi-\pi^*$ excitation of the polaron structure in PANI appeared.³² The polymerization proceeds in Nylon-6 matrix with absorbance maximum shifting to 780 nm and later to 760 nm. Importantly, absorbance at 290 nm which is due to ANI disappears while polymerization proceeds. Mechanism of the polymerization is similar to interfacial polymerization and is controlled by diffusion of oxidant into Nylon-6 matrix saturated with ANI. Front of persulfate meets ANI first on the surface and then proceeds deeper into the film. So, layer of PANI starts to form on the surface and while persulfate diffuses becomes surrounded by oxidant. Hypsochromic shift of PANI peak thus is probably due to partial oxidation of emeraldine to pernigraniline.

Morphology of PANI/Nylon-6 films was investigated by AFM. Nylon-6 films being saturated in aqueous ANI solution (0.38 M) were placed in acidic (0.1 M HCl) solution of ammonium persulfate (4×10^{-3} M). The films were taken out and dried after defined periods of time to monitor the morphology changes during the polymerization. AFM micrographs of PANI/Nylon-6 composite film surface and initial Nylon-6 are shown in Figure 4. Pristine

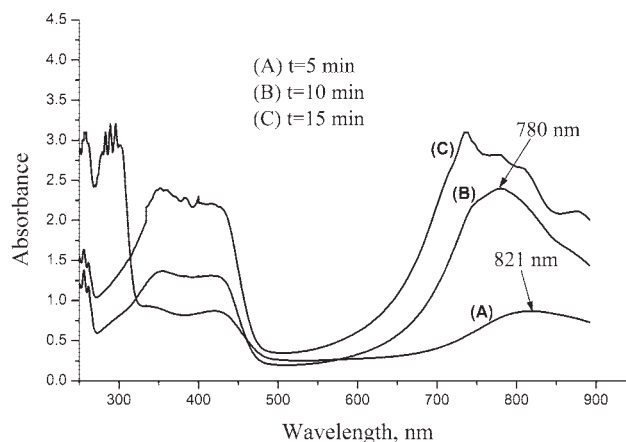


Figure 3 UV-spectra of PANI/Nylon-6 composite films prepared by polymerization in Nylon-6 matrix. $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 4.0 \times 10^{-3}$ M; (A) $t = 5$ min, (B) $t = 10$ min, (C) $t = 15$ min.

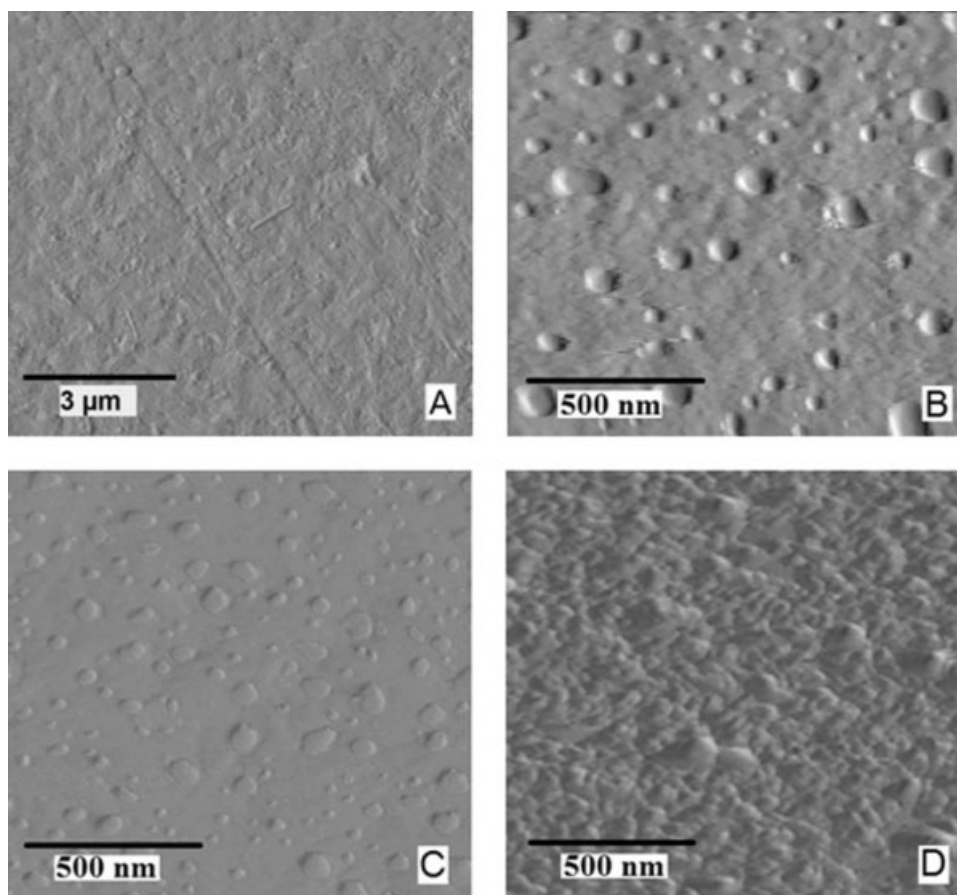


Figure 4 AFM images of PANI/Nylon-6 composite films surface. Polymerization in Nylon-6. $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 4.0 \times 10^{-3} \text{ M}$, $\text{pH} = 1$, $T = 20^\circ\text{C}$, (A) $t = 0 \text{ min}$ (pristine Nylon-6), (B) $t = 20 \text{ min}$, (C) $t = 40 \text{ min}$, (D) $t = 60 \text{ min}$.

Nylon-6 film is flat [Fig. 4(A)]. After 20 min of the polymerization PANI particles are clearly seen on the Nylon-6 surface [Fig. 4(B)]. The particles are spherical, about 50–150 nm in diameter and separated from each other in the Nylon-6 matrix. The area occupied by PANI particles is low. The concentration of PANI particles increases with time, while the size seems to remain unchanged [Fig. 4(C)]. Finally, continuous layer of PANI particles of the same size covers the Nylon-6 surface [Fig. 4(D)]. Interestingly, in the traditional solution polymerization, larger particles with diameter 200–500 nm are formed and the size is dependent on the polymerization time.³³

The electronic and ionic conductivities were measured by applying direct (DC) and alternating (AC) currents to the films, DC gives the electronic conductivity and AC the total conductivity (electronic and ionic). Initial Nylon-6 film had conductivity $5 \times 10^{-7} \text{ S/cm}$. The increase of the total and electronic conductivities on the polymerization time is shown on Figure 5. Within the first 40 minutes the conductivity was low and close to initial Nylon-6 film conductivity. Significant increase was observed on 40–60 minutes when continuous PANI layer appears on the surface [Figure 4(C)]. The final conductivity of

the PANI/Nylon-6 composite films was much lower ($\sim 10^{-3} \text{ S/cm}$) than conductivity of PANI powders ($\sim 1 \text{ S/cm}$).³⁴ Contribution of ionic (protonic) conductivity to the total conductivity was very small.

It is well-known that conductivity of the PANI strongly depends on doping (protonation) level.³⁵

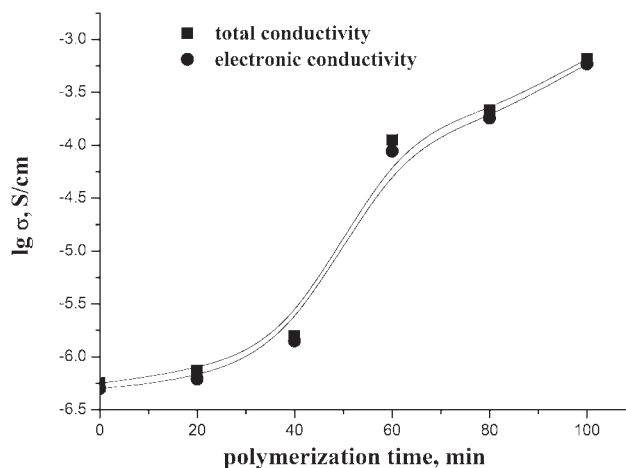


Figure 5 Conductivity dependence of PANI/Nylon-6 composite films prepared by polymerization in Nylon-6 matrix on polymerization time.

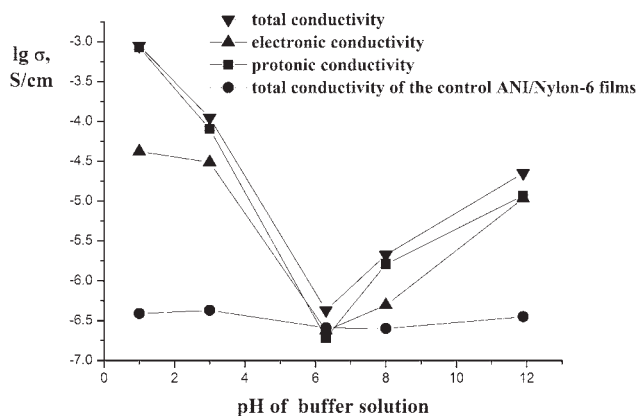


Figure 6 Conductivity of the PANI/Nylon-6 composite films after treatment in different buffers.

The PANI/Nylon-6 composite films prepared by 1 hour ANI polymerization in 4.0×10^{-3} M solution of ammonium persulfate were immersed in buffer solutions with different pH values for 24 hours for a systematic control of the degree of protonation. As a control Nylon-6 films saturated with ANI monomer were placed in the same buffers. Before conductivity measurements all films were kept at 80% humidity for 24 hours. Dependence of total, electronic and protonic conductivity on pH of buffer solution is shown on Figure 6. Film being immersed in buffer solution with pH = 1 showed high ionic conductivity and protonic conductivity was dominant throughout whole pH range, perhaps due to adsorption of additional protons by Nylon-6 matrix. While the pH value increased, conductivity decreased and minimum was observed at pH = 6.15, at this pH value PANI was fully deprotonated and nonconductive. Increase of ionic conductivity up to 10^{-5} S/cm in alkaline media is probably attributed to hydroxyl ion adsorption. In control experiment all ANI/Nylon-6 films showed conductivity of the initial Nylon-6 level (10^{-6} to 10^{-7} S/cm).

CONCLUSIONS

PANI has the desired stable electrical properties but lacks the mechanical appearance needed for a stand-alone device. We have prepared PANI and Nylon-6 composite films by oxidative polymerization of ANI in Nylon-6 matrix. The polymerization was shown to proceed optimally from aqueous ANI solutions. The morphology studies revealed formation of nano-size PANI domains on Nylon-6 surface which later during the polymerization fused into a continuous layer of PANI. As the ANI interactions with the matrix played an important role, we assume that PANI also interacts by hydrogen bonding with Nylon-6 matrix. As the projected potentiometric usage requires stability in aqueous medium, we followed

the behavior of the prepared films in various buffer solutions. It was shown that protonic conductivity is the dominant property of the PANI/Nylon-6 films in low pH region. With the increase of pH, conductivity decreases due to deprotonation. At high pH values, the subsequent increase in ionic conductivity can be related to the hydroxyl diffusion.

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