

Preparation, electrical properties and thermal stability of conductive polyaniline:nylon-6,6 composite films

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Abstract. The polyaniline:nylon-6,6 (PANI:Ny-6,6) composite films were prepared by diffusion process and the oxidative polymerization of aniline within the nylon-6,6 matrix. The composite films were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) as well as for their electrical properties. The surface electrical conductivity of the HCl (1 M) doped composite films increases with increase in the polyaniline content of the films. The study of electrical properties under isothermal conditions in the temperature range of 50–130°C showed that the composite films were stable under ambient conditions below 90°C in terms of DC electrical conductivity retention.

Keywords: polymer composites, electrical properties, thermal stability

1. Introduction

There is an explosive increase in the demand for composite materials in the last two decades, which are now available as materials with unique combination of properties. The electronic and optical properties of conducting polymer and insulating polymer matrix combined with attractive mechanical properties and processing advantages of the polymers has now attained a level of maturity consistent with a new set of opportunities to develop a wide range of application based conducting polymer composites. Thus, the composites based on conducting polymers and insulating polymers have been studied as materials for industrial products, such as rechargeable batteries, conductive coatings, light emitting diodes, gas sensors and antistatic materials [1].

Polyaniline has been widely investigated due to its low cost, easy synthesis and high as well as tailorable electrical conductivity depending upon the level of doping, environmental stability and interesting redox properties [2–5]. In spite of its several

desirable properties, the insolubility in conventional solvents for processing [6] and poor mechanical strength limit its application [7].

One of the ways to overcome these demerits is to prepare conducting composites of polyaniline by chemical or electrochemical polymerization within an insulating polymer matrix [8, 9]. It is easy to control the chemical polymerization of aniline within the insulating polymer matrix to prepare conducting composites of required electrical properties while retaining the mechanical strength of insulating polymer matrix [10–12]. In this paper, we have reported a simple chemical route to prepare polyaniline:nylon-6,6 composite films. Nylon-6,6 is one of the most popular materials used as fibers and thermoplastics.

2. Experimental

2.1. Reagents and chemicals

The main chemicals used, for the preparation of composite films were: aniline, 99% (CDH, India),

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Table 1. Preparation details of polyaniline:nylon-6,6 composites

Sample ID	Temp [°C]	Time [h]	Weight of nylon-6,6 films [g]	Amount of aniline soaked [g]	Weight of film after soaking [g]	Weight of films after polymerization [g]
PANI:Ny-6,6-(1)	80	10	0.2658	0.0225	0.2883	0.2984
PANI:Ny-6,6-(2)	80	15	0.2658	0.0450	0.3108	0.3217
PANI:Ny-6,6-(3)	80	20	0.2658	0.0675	0.3323	0.3450
PANI:Ny-6,6-(4)	80	25	0.2658	0.0910	0.3558	0.3682
PANI:Ny-6,6-(5)	80	30	0.2658	0.1125	0.3783	0.3916
PANI:Ny-6,6-(5a)	80	30	0.1627	0.0138	0.1765	0.2396
PANI:Ny-6,6-(5b)	80	30	0.1694	0.0148	0.1842	0.2416
PANI:Ny-6,6-(5c)	80	30	0.1794	0.0156	0.1960	0.2643

nylon-6,6 (from Research, Design and Standard Organization), hydrochloric acid, 35% (E. Merck, India), potassium persulphate, 98% (CDH, India).

2.2. Preparation of polyaniline:nylon-6,6 composite films

Square shaped pieces of 0.265 g each were cut from nylon-6,6 sheet and then pressed into thin films by applying pressure of 10 tons in an Electrically Operated Automatic Pressure Machine maintained at a temperature of 220°C. The thickness of films varied in the range of 0.40 to 0.50 mm. Each film was kept for soaking in 30 ml of doubly distilled aniline for different periods of time in an air oven at 80°C to allow aniline diffuse into nylon-6,6 matrix. Aniline soaked films were treated with 0.1 M potassium persulphate in 1 M HCl solution and left for 24 hours at ice temperature in order to polymerize aniline within the nylon-6,6 matrix. Thus prepared polyaniline:nylon-6,6 composite films were washed with doubly distilled water up to acid neutralization and undoped by treatment with excess of aqueous ammonia (1 M) followed by washing with distilled water until the filtrate became neutral. The composite films were dried for 24 hours at 40°C in a dry box and then stored in desiccators for experiments. Polyaniline:nylon-6,6 composite films were doped by treating with 1 M HCl solution at room temperature for 24 hours. The preparation details are given in Table 1.

2.3. Testing methods

For the study of the difference in surface morphology between the parent materials and their composites, SEM micrographs were taken by LEO-435 VP SEM instrument. FTIR spectra of polyaniline:nylon-6,6 composites were recorded by Nicolette-Protégé 460. DC electrical conductivity of the

doped composites films was measured with increasing temperature by using a four-in-line probe technique. DC electrical conductivity (σ) was calculated using Equations (1) and (2):

$$\rho = \frac{\rho_0}{G_7(W/S)} \quad (1)$$

$$\sigma = \left(\frac{1}{\rho} \right) \quad (2)$$

where σ , ρ , ρ_0 , W and S electrical conductivity [S/cm], corrected resistivity [Ω ·cm], uncorrected resistivity [Ω ·cm], thickness of the film [cm] and probe spacing [cm] respectively [13]. $G_7(W/S)$ is a correction divisor, which is a function of thickness of the sample as well as probe spacing. The sample to be tested is placed on the base plate of four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure is applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in electrically controlled oven. The current was passed through the outer probes and the floating potential across the inner pair of probes was measured. The power supply of the oven was then switched on, the temperature was allowed to increase gradually. The current and voltage were recorded simultaneously with a rise in the temperature.

The thermal stability of composite samples in terms of DC electrical conductivity retention was studied under isothermal conditions by using four-in-line DC electrical conductivity measuring instrument. This study was carried out at 50, 70, 90, 110 and 130°C on the selected composite films. The electrical conductivity measurements were done at an interval of 10 min.

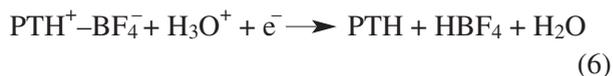
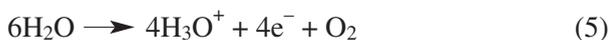
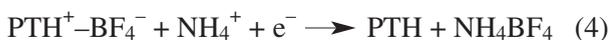
3. Results and discussion

3.1. Preparation of conducting polymer composite films

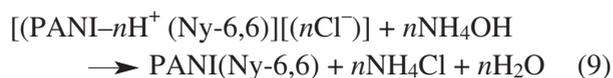
The preparation of polyaniline:nylon-6,6 composite films was done by diffusing of aniline into nylon-6,6 matrix. During this process, some amount of nylon-6,6 was dissolved in aniline producing jelly like precipitate above 80°C as well as if kept in aniline for more than 30 hours at 80°C. Therefore, the temperature and duration of soaking of aniline within the nylon-6,6 matrix were selected at 30 hours and 80°C respectively. The composition of composite films for the determination of variation in electrical conductivity of the composite films, due to the change in amount of nylon-6,6, four different samples were prepared as same temperature and time. Hence, a number of HCl doped polyaniline:nylon-6,6 composite film samples were prepared as detailed in Table 2.

When aniline is oxidized with 0.1 M potassium persulphate (K₂S₂O₈) in acidic media (HCl), the protonated conducting form of polyaniline (emeraldine salt) is produced with black color [14].

Schöllhorn and Zagefka [15] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which has been further supported by the work of Foot and Shaker [16]. On the basis of disproportionation reaction of ammonia as suggested by Mohammad [17] for the undoping of polythiophene (PTH) by water. The overall chemical reactions are given in Equations (3)–(7):



The charge neutralization reaction depends on the rate of chemical reaction between the doped polymer and undoping agent, which depends upon the reactivity of the polymer chain and basic strength of undoping agent [17]. The basic strength of water is very low, hence, it does not act as an effective undoping agent in the case of polyaniline, however, an analogous neutralization reaction for the undoping of the polyaniline component of the composites by ammonia solution may be suggested as shown by Equations (8) and (9):



Recently, it has been reported that PANI:Ny-6 composite film consisted of layers, the outer layers were conducting composite layers and the inner layer was pristine nylon-6 [18]. In a similar way, it seems that polyaniline is mainly polymerized in the outer layer of the composite film (PANI:Ny-6,6) and this layers retards the diffusion of the oxidant solution to the interior side and prohibits polyaniline from being polymerized inside the film or aniline does not diffuse deep inside the polymer matrix as observed in the cross-sectional view of the films.

3.2. Characterization

3.2.1. SEM studies

Figure 1 shows the SEM photographs of polyaniline, nylon-6,6 and polyaniline:nylon-6,6 compos-

Table 2. Preparation details of HCl doped polianiline:nylon-6,6-(5) composite films

Sample ID	Amount of aniline soaked [%]	Color		σ [S/cm]
		As-prepared	HCl doped	
PANI:Ny-6,6-(1)	08.4	light green	light brown	very low
PANI:Ny-6,6-(2)	16.9	light green	light brown	very low
PANI:Ny-6,6-(3)	25.3	green	dark brown	~10 ⁻⁵
PANI:Ny-6,6-(4)	33.8	green	black	~10 ⁻³
PANI:Ny-6,6-(5)	42.3	dark green	black	~10 ⁻¹
PANI:Ny-6,6-(5a)	42.3	dark green	black	0.121·10 ⁻¹
PANI:Ny-6,6-(5b)	42.3	dark green	black	0.262·10 ⁻¹
PANI:Ny-6,6-(5c)	42.3	dark green	black	0.134·10 ⁻¹

ite at different magnifications. Evidently, the homogeneous formation of composites of polyaniline in the nylon-6,6 matrix is observed. The surface morphology of chemically prepared PANI showed a cloudy structure while that of nylon-6,6 is somewhat granular and the morphology of composite film is totally different from their parent compounds i. e. PANI and nylon-6,6. The difference in surface morphology of composite indicates the binding of the parent component consequently, the formation of a composite.

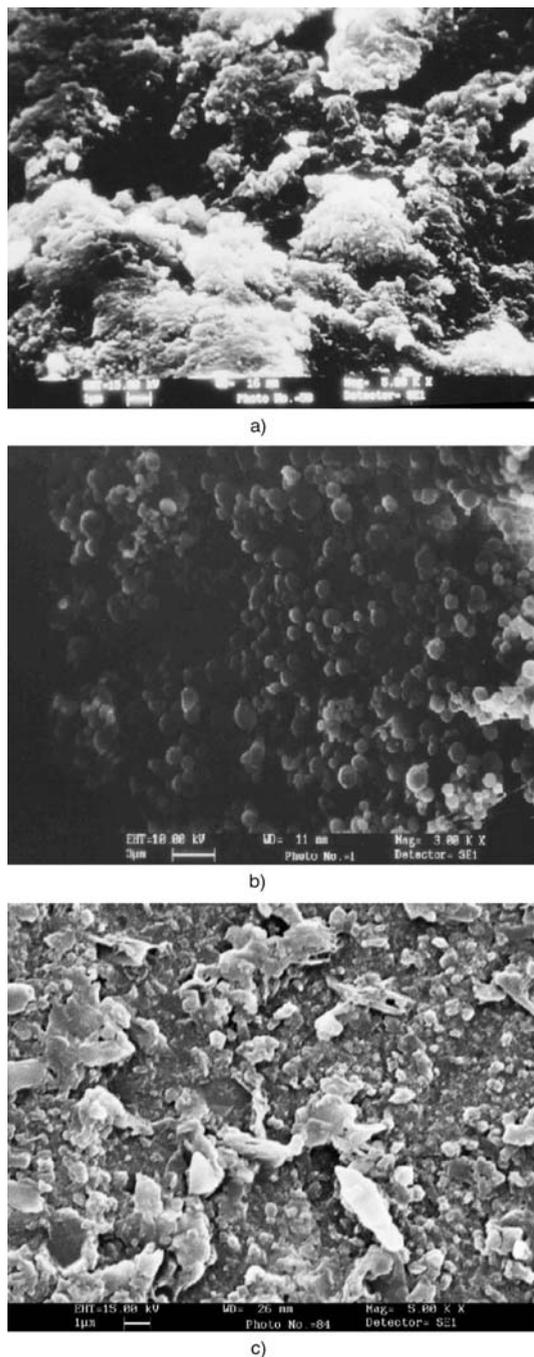


Figure 1. SEM photograph of a) polyaniline, b) nylon-6,6 and c) of PANI:Ny-6,6-(5) composite film

3.2.2. FTIR studies

The FTIR spectra of polyaniline:nylon-6,6 composites are presented in Figure 2. The band corresponding to out of plane bending vibration of C–H bond of p-disubstituted benzene rings appears at 824 cm^{-1} . The bands corresponding to stretching vibration of N–B–N and N=Q=N structures appear at 1497 cm^{-1} and 1587 cm^{-1} respectively where –B– and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C–N bond appear at 1143 and 1302 cm^{-1} . The band close to 1130 cm^{-1} is described as being characteristic of the conducting polymer due to the delocalization of electrical charges caused by deprotonation. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the polyaniline. The characteristic bands at around 688 , 1642 , 3303 cm^{-1} attributed to nylon-6,6 are present in all the composites. As-prepared polyaniline: nylon-6,6 composite showed a strong

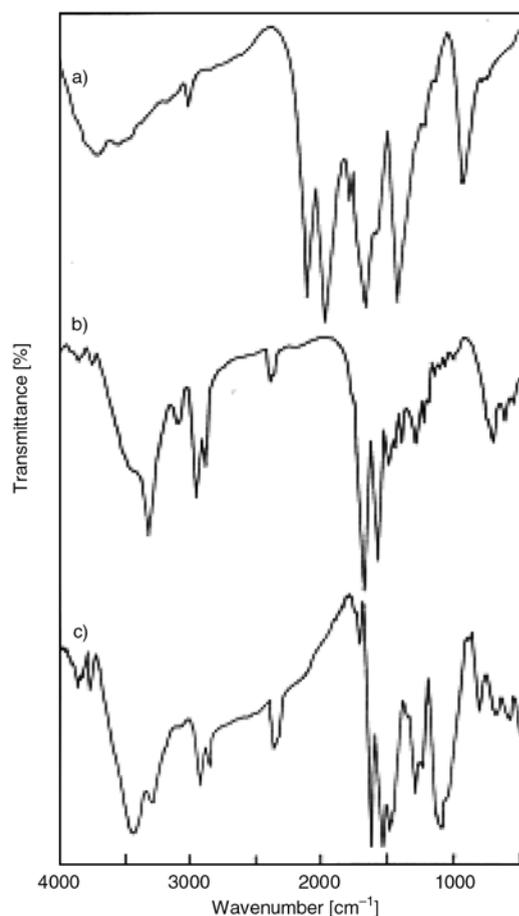


Figure 2. FTIR spectra of polyaniline:nylon-6,6 composite films. a) PANI:Ny-6,6-(3), b) PANI:Ny-6,6-(4) and c) PANI:Ny-6,6-(5)

band around 1650 cm⁻¹ corresponding to carbonyl group of nylon-6,6. For polyaniline, the band corresponding to out of plane bending vibration of C–H bond of p-disubstituted benzene ring appears around 824 cm⁻¹. The bands corresponding to stretching vibration of N–B–N and N=Q=N structure appear around 1377 cm⁻¹ and 1500 cm⁻¹ respectively (where –B– and =Q= stand for benzenoid and quinoid moieties in the polymer). The band corresponding to stretching mode of C–N bond appears at 1504 cm⁻¹ [19]. The gradual increase in the intensities of the bands corresponding to polyaniline and decrease in the intensities of bands corresponding to nylon-6,6 support the gradual change in the composition of the composite samples.

3.2.3. Stability in terms of DC electrical conductivity retention

Three samples, PANI:Ny-6,6-(3), PANI:Ny-6,6-(4) and PANI:Ny-6,6-(5) were selected for the study of thermal stability in terms of DC electrical conductivity retention. It was observed that the electrical conductivity of PANI:Ny-6,6 composites increased on exposure to HCl, due to doping of polyaniline component of the composite films, as evident from Equation (10) [20, 21]:



The isothermal stability testing of the HCl doped films in terms of DC electrical conductivity retention was carried out at 50, 70, 90, 110 and 130°C in an air oven. The electrical conductivity measurements were done at an interval of 10 minutes in the accelerated ageing experiments. The electrical conductivity measured with respect to time of accelerated ageing is presented in Figure 3. The thermal stability was also studied by repeatedly measuring DC electrical conductivity with increasing temperature from 30 to 130°C for five times at an interval of 40 minutes.

The electrical conductivity of the polyaniline:nylon-6,6 films was measured from 30 to 130°C and found to be in the semi-conducting region. All the composite films followed the Arrhenius equation for the temperature dependence of the electrical conductivity from 30 to 115°C. After that a deviation in electrical conductivity was observed.

A combination of all or some of the following factors could be responsible for the decrease in electrical conductivity beyond 130°C such as the loss of dopant and degradation, the chemical reaction of dopant with polyaniline or nylon-6,6, the semi-conductor to metal transition and the approaching of *T_g*. The studies on the stability of electrical conductivity under isothermal conditions at 50, 70, 90, 110 and 130°C showed that the electrical conductivity is stable at 50, 70 and 90°C supporting the fact that all the composite films were sufficiently stable in term of DC electrical conductivity retention under ambient conditions below 90°C and the electrical conductivity decreases with respect to time at 110 and 130°C may be attributed to the loss of dopant. The stability in terms of DC electrical conductivity retention was observed to be fairly good as studied

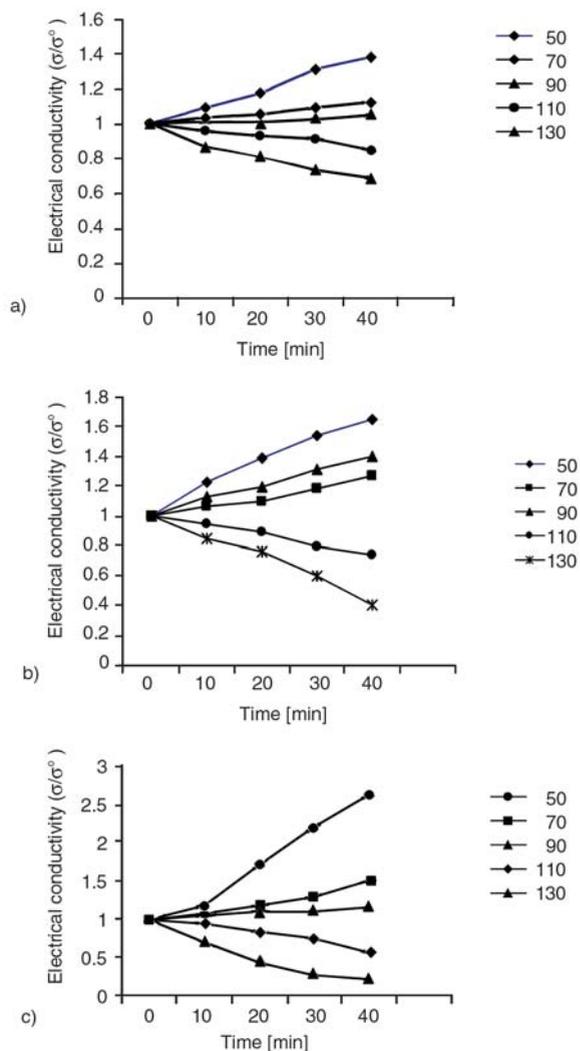


Figure 3. Stability in terms of DC electrical conductivity retention under isothermal conditions at 50, 70, 90, 110 and 130°C. a) PANI:Nylon-6,6-(3), b) PANI:Nylon-6,6-(4) and c) PANI:Nylon-6,6-(5)

by isothermal technique. The polyaniline:nylon-6,6 composite films were found to be suitable for use in electrical and electronic applications below 90°C under ambient conditions.

4. Conclusions

The preparation of conductive polyaniline:nylon-6,6 composite films is very successfully demonstrated by diffusion of aniline monomer into the nylon-6,6 matrix followed by oxidative polymerization of aniline within the nylon-6,6 matrix technique. Thus prepared polyaniline:nylon-6,6 composite films possess high electrical conductivities at higher doping levels. It is also observed that the electrical conductivity of polyaniline:nylon-6,6 films increases with increase in polyaniline content of the composite. The composite material was successfully characterized for their electrical properties, FTIR and SEM. Thermal stability in terms of DC electrical conductivity retention is fairly good as studied by several experimental techniques. Most of the formulations of the composites so prepared are suitable for use in electrical and electronic applications below 90°C under ambient conditions.

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