

# Ac and Dc conductivities of polyaniline/poly vinyl formal blend films

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## Abstract

The synthesis and characterization of polyaniline (PANI)/poly vinyl formal (PVF) blend films were carried out in this work. Polyaniline base was doped using dodecylbenzene sulfonic acid (DBSA). These blend films were characterized by UV–Visible, FTIR spectra and scanning electron microscopy (SEM) to investigate their optical, structural and morphological properties. It was found that the percolation threshold of these blends is 4.4 wt% of PANI. The dc and ac conductivities of these blend films have been measured at a temperature range from 300 to 100 K in the frequency range of 10 kHz to 1 MHz. The electrical conductivity of the blend films enhanced with the increase of polyaniline amount up to a value of  $2.5 \times 10^{-4} \text{ S cm}^{-1}$  at 65 wt% of polyaniline. The dc conductivity of the PANI/PVF blend films follows the three-dimension variable range hopping. Temperature variation of frequency exponents in this blend suggests that ac conduction is attributed to be correlated barrier hopping.

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## 1. Introduction

Recently, polymers containing conjugated  $\pi$ -electron systems like polyaniline, polypyrrole and polythiophene have been well studied. Polyaniline has a special interest, within the field of conducting polymers for many reasons such as low monomer cost, a wide range of applications, simple polymerization methods, and a high yield of polymerization product. In the other side, polyaniline can not be processed by the simple routinely methods used in the plastic industry and pure polyaniline has poor mechanical properties [1]. Doping of polyaniline with functionalized organic acids, such as DBSA, *p*-toluene sulfonic acid, and camphor sulfonic acid (CSA) improves its solubility in common solvents [2,3].

The blending of PANI with other conventional polymers such as PMMA, nylon 6, PVC and cellulose triacetate is a very active area, since combined good mechanical properties with high electrical conductivity can be attained [4–7]. Such blending will allow the use of PANI for medical application and sensors [8,9]. There are four routes for the blending preparation [5,10]:

- (1) Dispersions blending in which PANI/polymer blends can be obtained by simple mixing of the aqueous PANI dispersion with an aqueous emulsion of the matrix polymer followed by water evaporation.
- (2) Melt blending in which binary and ternary blends are prepared by melting the mixture in a Brabendar.
- (3) Solution blending in which the two constituents of the blend (conductive and insulating) dissolve in a common solvent followed by solvent evaporation.
- (4) *In situ* oxidative polymerization of aniline monomer in the polymeric matrix.

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Low percolation threshold is one of the most interesting features of PANI blends. The charge transport mechanisms of these new percolating media have a paramount fundamental interest. The temperature and frequency dependent studies of these blends are very useful in order to obtain better understanding of the charge transport mechanism for these percolating media [11].

PVF has a high softening point, excellent electric insulation characteristic, high flexibility and good abrasion resistance and so has diverse applications, including wire insulation, coatings for musical instruments, adhesives and support films for electron microscopy [12,13]. The purpose of this work is the preparation of the blend films having the synergistic properties of both PVF and PANI. PANI/PVF blend has been prepared by Lei et al. [14]. In their study, an *in situ* polymerization technique was used to obtain pseudo-IPN system with a conjugated linear conducting PANI in a crosslinked PVF or PMMA matrix. The transformation from insulator to conductor took place at aniline weight ratio of about 0.2. In this article, PANI/PVF blend films are prepared using a solution blending method to obtain lower percolation threshold. Optical, structural, morphological and electrical properties of the blend films are studied. The ac and dc conductivities and conduction mechanisms of this blend in the temperature and frequency ranges of 100–300 K and 10 kHz–1 MHz, respectively, are measured and discussed.

## 2. Experimental work

### 2.1. Materials

Aniline (Loba Chemie, India) was purified by vacuum distillation before use. Ammonium persulphate and poly vinyl formal (formavar) was purchased from Aldrich. Dodecylbenzene sulfonic acid (DBSA) was obtained from Oil Extractor Company (Egypt). The chloroform, methanol, and diethyl ether solvents were bought from El-Gomhory Chemical Company (Egypt).

### 2.2. Synthesis of polyaniline

The chemical polymerization of aniline was carried out in an aqueous acidic solution where ammonium persulphate (54 g) was dissolved in 900 ml of 1.2 M HCl (previously cooled to 0 °C). Aniline (80 ml) was also dissolved in 1000 ml of precooled 1.2 M HCl. Acidic solution of the ammonium persulphate (oxidant agent) was then slowly added to aniline solution for one hour to prevent the temperature exceeding 5 °C. The mixture was then left for 3–4 h with continuous stirring. After that, the precipitated polyaniline hydrochloride was filtrated and washed consecutively with distilled water, methanol, and diethyl ether. The polyaniline hydrochloride was dried at 50 °C for 48 h. Polyaniline base was obtained by adding 3%

ammonia solution for 2 h to polyaniline hydrochloride. Deprotonated polyaniline was then separated, washed and dried in the same manner as above.

### 2.3. Preparation of polyaniline/poly vinyl formal blend films

The polyaniline base (EB) was pasted with DBSA with 1:2.5 weight ratio and then dissolved in chloroform. The PVF was also dissolved in chloroform. The blend films of PANI/PVF with different weight percentages of polyaniline were cast at 60 °C on glass slides.

### 2.4. Characterization

Polymeric blend films prepared were put onto KBr disks for FTIR measurements. Spectra were carried out with a (Shimadzu 8400 S) FTIR spectrophotometer. UV–Visible spectra were obtained using a Lambda 25 spectrophotometer; the spectra were obtained directly by inserting the polymeric films in the spectrophotometer cell compartment, and studied over the wavelength range between 200 and 1000 nm. Scanning electron micrographs were obtained by JEOLJSM 6360LA for blend films coated with a thin layer of gold. The dc conductivity was measured at different temperatures (100–300 K) using cryogenic system. The PANI/PVF blend films pasted with Ag were mounted between the two copper electrodes for dc conductivity measurements. Keithley 616 electrometer was used for measuring the electrical resistance of the blend films. The bulk conductivity ( $\sigma_m$ ) was calculated using the following equation:

$$\sigma_m = 1/\rho = 1/(RA/d) \quad (1)$$

where  $\rho$  is the resistivity,  $R$  is the electrical resistance,  $A$  is the area of electrode, and  $d$  is the thickness of the sample.

For ac conductivity measurement, the films were coated on two opposite sides with silver paint. The measurements were carried out with Hewlett Packard 42277A LCZ meter in the frequency range of 10 kHz–1 MHz over the temperature range 100–300 K.

## 3. Results and discussion

### 3.1. FTIR and UV–visible spectra

Fig. 1 represents the FTIR spectra of PANI-DBSA/PVF blend films at 0.0 (a), 5 (b) and 20 (c) weight percentages of PANI. The bands at 1180, 1135, 1070 and 1020  $\text{cm}^{-1}$  are related to C–O–C–O–C stretching vibrations of PVF. The C–H stretching bands are characteristic of formal group and appear at 3050, 2950, and 2850  $\text{cm}^{-1}$  as shown in Fig. 1a [15]. On the other hand, the bands around 1600, 1490, 1250, 1170, 1030 and 806  $\text{cm}^{-1}$  correspond to polyaniline in the blend films as shown in Fig. 1b and c. The band corresponding to out of plane bending vibration of C–H bond of *p*-substituted benzene ring appears at 806  $\text{cm}^{-1}$ . The bands corresponding to stretching vibrations of N–B–N and N=Q=N structures appear around

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