The Effect of Oxalic Acid as a Doping Agent on the Conductivity of Polyaniline

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ABSTRACT

This study investigates the effect of oxalic acid at different concentrations as doping agent on the electrical properties of polyaniline (PANI). The polymerization of aniline to produce PANI was carried out in media containing oxalic acid at 0.08 M, 0.09 M, 0.1 M, 0.2 M and 0.3 M in the presence of ammonium persulphate as oxidizing agent. The successful formation of PANI doped with oxalic acid was confirmed by FTIR and the morphology studied using XRD. An impedance investigation on the series of PANI formed revealed that doping in 0.1M oxalic acid produced PANI of the highest conductivity of 2.52 x 10^{-6} Scm^{-1}.

Keywords: *polyaniline, oxalic acid, conductivity, impedance spectroscopy*

INTRODUCTION

Polyaniline (PANI) behavior is affected by the type of acid used during its preparation [1]. PANI is more conductive when doped with acid [2]. The commonly used acids are sulphuric acid, hydrochloric acid, phosphoric acid and benzenesulfonic acid. Preparation of oxalic acid as dopant and ammonium persulphate as the oxidant in the polymerization was first reported by Chuanyu and co-workers [2]. The conductivity of polyaniline is due to the presence of conjugated double bonds along the backbone of the polymer. The presence of the conjugated double bonds allows electrical charges to migrate a long distance [3]. The conductivity behaviour of polyaniline is affected by the type of acid used as well as its molar ratio towards aniline during the polymerization [2]. This paper reports the effect on electrical properties of polyaniline of different oxalic acid concentrations when used as doping agent.

MATERIALS AND METHODS

Materials

Ammonium persulphate (Merck), aniline (Systerm) and oxalic acid (R&M chemicals) were used as received for the preparation of polyaniline. All the chemicals used were of analytical grade. 0.08 M, 0.09 M, 0.1 M, 0.2 M and 0.3 M oxalic acid was prepared by dilution with double distilled water.

Methods

PANI doped oxalic acid was prepared by chemical oxidative polymerization of aniline in media containing oxalic acid at 0.08 M, 0.09 M, 0.1 M, 0.2 M and 0.3 M in the presence of ammonium persulphate as oxidizing agent [2]. The green precipitate of PANI salt was filtered and rinsed with water. The polymerized samples were characterized using FTIR (Perkin Elme Fourier Spectroscopy) in the region between 4000 cm^{-1} to 500 cm^{-1} and XRD (XPert PRO). The conductivity of these samples was determined using impedance spectroscopy (Gamry EIS 300 potentiostat). For determination of electrical properties of PANI, impedance measurements were performed by sandwiching the sample between two stainless steel electrodes of 0.9 cm diameter. Impedance was measured from 100 MHz to 1 Hz using sinusoidal wave of 10 mV at room temperature. The conductivity of the membranes was calculated using the bulk resistance (R_b) value from the Nyquist plot.

The ionic conductivity (σ) was calculated using Equation 1 [4]:

$$\sigma = \frac{d}{AR_b} \qquad (1)$$

where d is the sample thickness, A is the cross sectional area of the sample and R_b is the bulk resistance.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR)

Figure 1 shows the infrared absorption of PANI, oxalic acid and aniline. FTIR was conducted to determine the interactions that occur between polyaniline and oxalic acid. The disappearance of two ν(N-H) peaks attributable to primary amine in the region 3500 to 3200 cm^{-1} in PANI spectrum suggested the successful polymerization of aniline as shown in the reaction in Figure 2. The ν(C=C) peak at 1579 cm^{-1} is due to the vibration in quinone ring whereas the peak at 1496 cm^{-}1 is characteristic of ν(C=C) in benzene ring. The ν(C-N) band of quinone ring is observed at 1297 cm^{-1}. The peak at 1123 cm^{-1} is noted as the peak of (NH^+) structure, and is associated with the conductivity behavior of polyaniline [5]. A peak is also observed at 1247 cm^{-1}, which related to the vibration of C-O in the polymeric structure. The peak at 820 cm^{-1} is attributed to the plane bending vibration peak of C-H in disubstituted benzene.

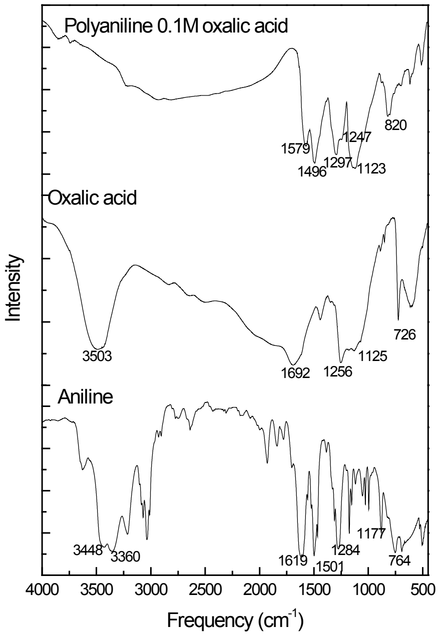

Figure 1: Infrared spectra of PANI, oxalic acid and aniline

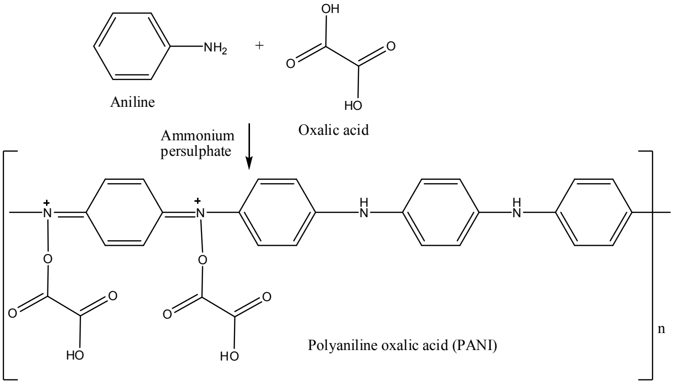

Figure 2: Formation of PANI from the reaction of oxalic acid and aniline in the presence of ammonium persulphate as oxidizing agent

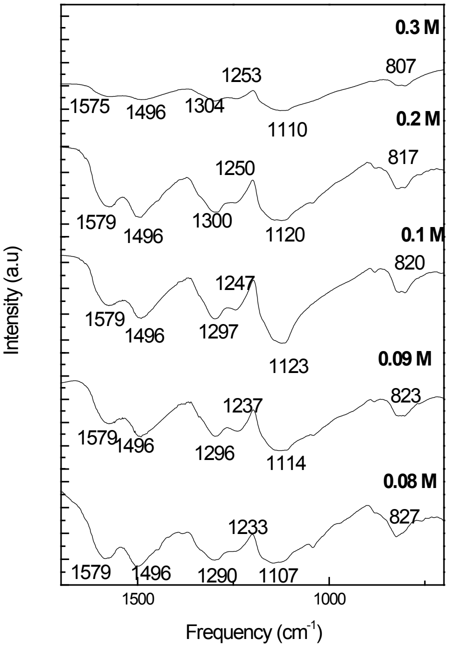

Figure 3: Infrared absorbance of PANI doped with different concentrations of oxalic acid a) 0.3 M, b) 0.2 M, c) 0.1 M, d) 0.09 M and e) 0.08 M

Figure 3 illustrates infrared spectra of PANI doped with different concentrations of oxalic acid a) 0.3 M, b) 0.2 M, c) 0.1 M, d) 0.09 M and e) 0.08 M. The peaks in the region of 1496 cm^{-1} are due to the ν(C=C) of quinone and benzene ring in polyaniline. The peak becomes better defined with the dilution of oxalic acid even though no shifting is observed. The peak at 1290 cm^{-1} can be assigned to the ν(C-N) in the quinone ring. The C-N absorbance shifted to a higher value as the concentration of oxalic acid increased. This depicted that the interaction of dopants agent appears at the C-N bond instead of at the polyaniline backbone chain. The vibrational mode of carboxyl (C-O) band at 1233 cm^{-1} (0.08 M oxalic acid) shows a significant shifting when the concentration of oxalic acid increased. It can be inferred that the oxalic acid has successfully doped into the polyaniline chain. The C-O peak intensity reduced as the concentration of oxalic acid increased. The peak intensity of ν(NH$^+$) at 1107 cm^{-1} increased as the concentration of oxalic acid was increased up to 0.1 M, beyond which the peak started to broaden. A shifting to a higher value was also observed. However, the value started to decrease when the acid concentration was higher than 0.1 M. This peak corresponds to the conductivity characteristic of polyaniline. This is consistent with the results reported by Trchová and Stejskal [5].

X- RAY DIFFRACTION (XRD)

The XRD spectra were recorded at 2θ (Figure 4). For polyaniline doped with 0.08 M and 0.09 M oxalic acid only two peaks can be observed. The two peaks at 20° and 25.7° can be attributed to the periodic vertical parallel structure in the main chain [6,7]. However, when polyaniline was doped with higher concentrations of oxalic acid (0.1 M, 0.2 M and 0.3 M), three peaks can be observed at 2θ = 15°, 20° and 25.7°. The prominent peak at 15° is due to the presence of doping agent which became closer to the N atom at the polymer main chain. At the highest concentration of 0.3 M, the peaks at 2θ = 15° and 20° are seen to become converged. These results show that the concentration of oxalic acid as doping agent has an effect on the polyaniline structure [7].

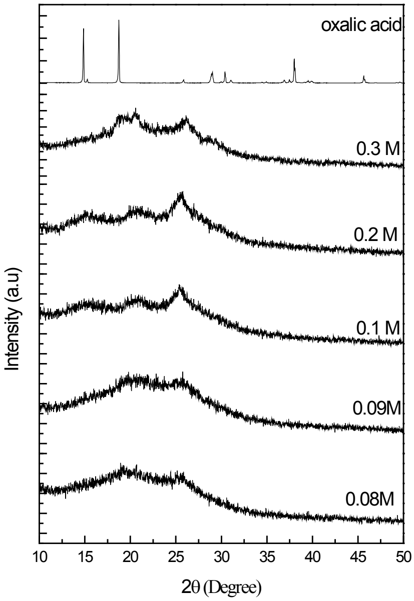

Figure 4: The X-Ray diffraction of polyaniline doped with different concentrations of oxalic acid

CONDUCTIVITY

The conductivity of polyaniline doped with different concentrations of oxalic acid is illustrated in Figure 5. It can be seen that the highest conductivity was 2.52 x 10^{-6} Scm^{-1} observed for the film produced in the presence of 0.1 M oxalic acid. The increase in conductivity at 0.1 M oxalic acid may be due to the increase of efficiency of charge transfer between the polymer chains and the dopant. The rise in conductivity value is supported by FTIR results in which the highest intensity of $\nu(NH^+)$ was observed at 0.1 M as well. FTIR results showed changes of the electronic distribution around the N atom, which play a major role in the conduction mechanism in this conducting polymer. However, conductivity declined with further increase of the oxalic acid concentration. The decline in conductivity may be due to the presence of too much oxalic acid at the polymer backbone, resulting in ionic congestion leading to decrease in conductivity. The conductivity value obtained is lower than that reported by Chuanyu *et al.* [2].

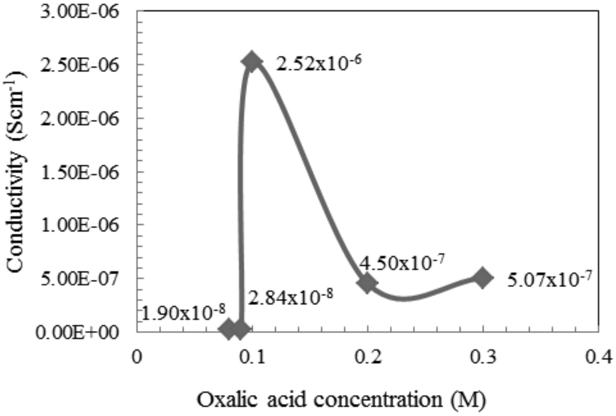

Figure 5: Conductivity value (Scm^{-1}) of polyaniline doped with different concentration of oxalic acid (0.08 M, 0.09 M, 0.1 M, 0.2 M and 0.3 M)

CONCLUSION

Polyaniline doped with different concentrations of oxalic acid were successfully synthesized and characterized. Infrared spectroscopy data suggested that oxalic acid has doped into the polyaniline chain through the interaction of N of aniline and O of oxalic acid, where the interaction of oxalic acid happens at the polyaniline backbone. XRD results indicated that oxalic acid concentration affects the polyaniline structure. Impedance measurements showed that oxalic acid concentration affects the conductivity of polyaniline with the highest conductivity observed at 0.1 M oxalic acid.

ACKNOWLEDGEMENT

The authors wish to acknowledge the Ministry of Higher Education, Malaysia for funding this work through Research Acculturation Grant Scheme (600-RMI/RAGS 5/3 (20/2014)) and the Faculty of Applied Sciences, UiTM for providing the scholarship and research facilities.

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