EFFECT OF DODECYLBENZENE SULFONIC ACID DOPANT CONCENTRATIONS ON THE SYNTHESIS OF POLYANILINE

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ABSTRACT: Modified physicochemical properties of polyaniline (PANI) colloids in response to various polymerization conditions are being made to enhance the electrical conductivity of PANI that can be used in supercapacitor purpose. In this paper, an attempt has been made to improve the mechanical stability of PANI by synthesizing with different concentrations (0.8, 1.65, 2.0, and 2.5 mmol) of dodecylbenzenesulfonic acid (DBSA). The DBSA doped PANI colloids were characterized by using XRD, Raman spectra and SEM. PANI containing 2.0 mmol of DBSA has the highest percentage of crystallinity (X_c %) as analyzed from XRD spectrum. Scanning electron microscopy (SEM) has been used to investigate the influence of the feed concentration of DBSA on the morphology of the polymer. A detailed study on the Raman spectroscopies of PANI-DBSA colloids has been carried out which shows that intensity of RAMAN spectra are directly proportional to the increased crystallized region of doped PANI samples; higher intensity may attribute due to the large change in polarization associated with the formation of covalent bond in PANI.

KEYWORDS: *Polyaniline; Raman; Advance Material; Dodecylbenzene; Sulfonic Acid*

1.0   INTRODUCTION

Electrical conductive polymer composites have major contribution in various applications such as electronics, telecommunications,

aerospace, security and, medical. Lately, conductive composites are designed as structural materials and also have more benefits compare to others materials used for cases, closures, conduit and electrostatic discharge protector [1-7]. In conductive polymer researches, polyaniline (PANI) has been focused as one of the prime material because it has higher conductivity once doped with acids and has a greater environmental stability. The primary application of PANI has been limited by its incompatibility nature, especially in the doped form. However, in the past few years, the improvement has been made in processing of doped PANI. There has been numeral research reports using functionalized protonic acid such as dodecyl benzene sulfonic acid (DBSA) to dope PANI and the possibility of processing in the conducting forms of PANI and blend with a polymer matrix [8-10]. Such preparation could be processed from a melt or from a solution mixture [11-13].

DBSA a prominent surfactant acts as a steric stabilizer and forms a small size colloidal particle, hence, it disperses excellently in an aqueous medium. DBSA also influences morphology of composite by altering the shape and size of PANI particles [12]. Novel synthetic methods for the preparation of PANI-DBSA by aniline oxidation polymerization in aqueous dispersion of the anilinium-DBSA complex have recently been reported [9, 12]. The synthesis method promotes to the formation of a stable emeraldine PANI salt. However, previous researches dealt with additional strong acid such as hydrochloric acid or sulphuric acid to control the acidic condition during polymerization process which may reduce the mechanical stability of the product.

In the present research, study is focused more on the DBSA effect without using strong acid to alter the acidic condition of PANI colloidal during polymerization. DBSA doped PANI colloidal was characterized using Scanning Electron Microscope (SEM), Raman Spectroscope (RS) and X-ray powder diffraction (XRD) and found that, during polymerization, DBSA can enhance the crystallinity of PANI colloidal.

2.0   METHODOLOGY

Aniline chloride and hydrochloric acid (37%) were collected from Merck, Ammonium peroxydisulfate and dodecylbenzene sulfonic acid were collected from Sigma-Aldrich.

The pristine PANI was synthesized (direct oxidation) by the polymerization of aniline hydrochloride (purum; 5.18g, 40mmol) and ammonium peroxydisulfate without addition of DBSA. The aniline hydrochloride and ammonium peroxydisulphate was dissolved separately in 100ml distilled water for each and both solutions were precooled at 9°C for 12 hours. The solutions were then mixed in a beaker, stirred slowly and left at rest to polymerize in a refrigerator at 9°C for 24 hours. While for DBSA doped PANI, aniline hydrochloride was added in different concentrations (0.8, 1.65, 2.0, and 2.5mmol) of aqueous DBS acid to prepare 100ml solution and ammonium peroxydisulphate was dissolved in distilled water to prepare 100ml solution. Both solutions were precooled (9°C, 12 hours) and were mixed in a beaker, stirred, and left at rest to polymerize in refrigerator at 9°C for 24 hours. Synthesised PANI precipitates (emeraldine salt) resultant from two different polymerisations were collected on filter papers, washed with 100ml of 0.2M HCl acid three times followed by final washing with100ml acetone. Later emeraldine salt was dried in vacuum oven at 60°C for 24 hours.

X-ray diffraction patterns of the powdered emeraldine salt samples were acquired by a PAN analytical's X-ray diffractometer using CuK α radiation window at angles from 10 to 40° (2θ) with step size of 0.05 degrees. For any polymer, percent crystallinity as obtained by X-ray measurements is defined as the ratio of intensity from the crystalline peaks to the sum of the crystalline and amorphous intensities. After peaks are assigned as crystalline or amorphous, the percent crystallinity is calculated by using the resolution of the peak, R is given by Equation (1) [14]:

$$R = \frac{m1 + m2 + \ldots + mn}{h1 + h2 + \ldots + hn} \tag{1}$$

where m_1, m_2 …are the heights of minima between two peaks, and h1, h2… are the heights of peaks from the base line. Hence for calculating percentage of crystallinity, all the peaks were considered.

Raman spectrums were obtained in the range of 900 to 1900 cm^{-1}. A weak green (514.5 nm) laser intensity is used, to avoid any perturbation of the samples. Polymer samples were coated with a thin layer of gold and placed under the scanning electron microscope

3.0   RESULTS AND DISCUSSION

3.1   XRD analysis

Emeraldine salt of PANI is partly crystalline and partially amorphous [15], so the changes in crystallinity can be determined from XRD patterns. The peaks of the XRD pattern are contributed by crystalline region. Therefore, by calculating area under the graph using equation 1, percentage of crystalline can be obtained. The XRD pattern of pristine PANI powder is shown in Figure 1 where the diffraction pattern of pristine PANI shows one broad and diffuse peak around 2θ= 210 indicating crystalline structure present in pristine PANI. The crystalline PANI phase is identified by the XRD peaks at 2θ angles of 15°, 21° and 25° which correspond to (011), (020) and (200) diffraction plane of PANI.
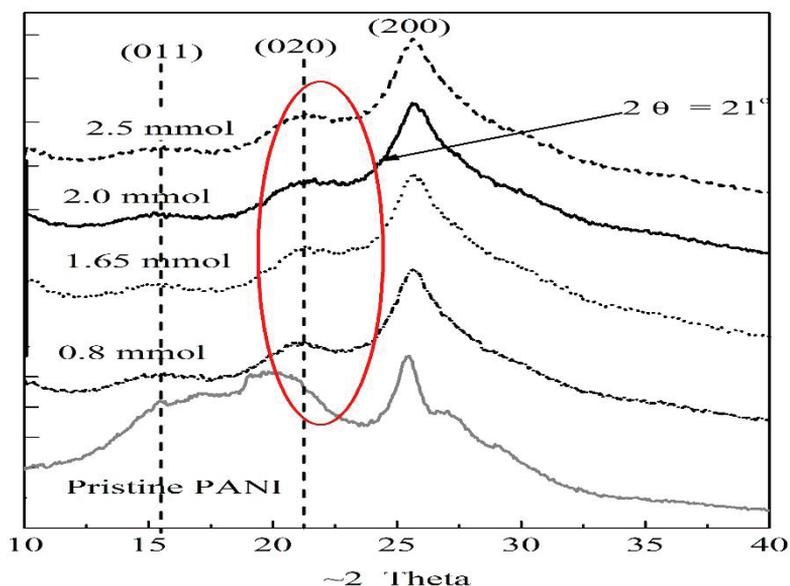
Figure 1: XRD patterns for pristine PANI, PANI doped with
0.8, 1.65, 2.0, and 2.5 mmol of DBSA

After doping, the peaks for PANI 0.8, 1.65, 2.0, and 2.5 DBSA show increasing in peak intensity and the peaks become broader which indicate doped PANI became more crystalline and the peaks are slightly shifted towards at lower angels as compared to the XRD pattern of pristine PANI. Percentage crystallinity (X_c %), as shown in Table 1 and constructed bar graphs in Figure 2 is calculated from area of 2θ. PANI 2.0 mmol of DBSA have the highest percentage of crystallinity (X_c %). The changes in percentage crystallinity for varying concentrations of DBSA acids were further correlated with Raman spectrums.

Table 1: Percentage of crystallinity, X_c (%) of pristine PANI and doped PANI

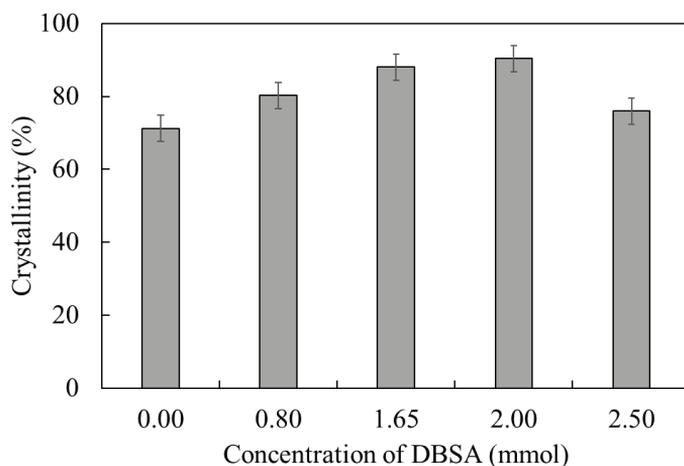| PANI powder	Xc (%)
Pristine PANI	71.2
PANI with 0.8 mmol DBSA	80.28
PANI with 1.65 mmol DBSA	88.08
PANI with 2.0 mmol DBSA	90.33
PANI with 2.5 mmol DBSA	75.94

Figure 2: Percentage of crystallinity X_c (%) of pristine PANI, PANI doped with 0.8, 1.65, 2.0, and 2.5 mmol of DBSA

3.2 Raman Spectroscopy analysis

The Raman spectra as shown in Figure 3 have three ranges corresponding to different vibration modes of PANI: C–H bending modes between 1100 and 1210 cm^{-1}, several C–N stretching modes (amines, imines and polarons) between 1210 and 1520 cm^{-1} and C–C stretching modes between 1520 (attribute to benzenoid C-C stretching modes) and 1650 cm^{-1} (attribute to quinoid C-C stretching mode) [17]. The covalent molecules (([C$_6$H$_4$NH]$_2$[C$_6$H$_4$N]$_2$)$_n$) present in PANI has the bonding electrons remain common to both nuclei, resulted to high intensity to Raman lines. Typically high crystalline material yields a spectrum with very sharp and intense Raman peaks, whilst an amorphous material will show broader and less intense Raman peaks. Therefore, the percentage of intensity is calculated using area under the spectrum to determine the correlation between concentrations of DBSA and crystallinity of synthesized PANI. Figure 4 shows the calculated value for percentage of intensity from the Raman spectra. When the concentration of DBSA increases from 0.8 to 1.65, the intensity is increased, however at 2.0 and 2.5 mmol, the intensity decreases. Since Raman activity is associated with a change in polarizability [18], therefore the higher intensity occurs due to the large change in polarization associated with the long-chain motion of crystalline mode. The PANI doped with 1.65 mmol of DBSA shows the highest intensity of Raman spectrum which may attribute to the large part of crystalline fraction of the PANI particles.
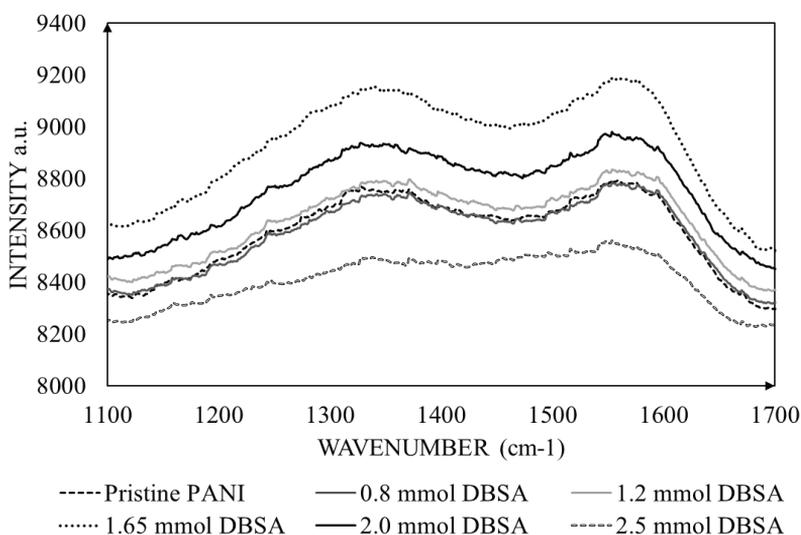
Figure 3: Raman Spectra of pristine PANI, PANI doped with 0.8, 1.65, 2.0 and 2.5 mmol of DBSA

However, at 2.0 and 2.5 mmol DBSA, the intensities are decreased. It may be due to high polarize molecule (from DBSA) present in doped PANI. The DBSA molecules consist of polar head and nonpolar tail that creates micelles in aqueous medium. Additional DBSA's molecules aggregate to form micelles in the bulk. The reaction mechanism which may contribute to crystallinity of the synthesized PANI doped with DBSA can be explained as shown in Figure 5. Initially, at low concentration of DBSA, PANI's molecules surrounded by DBSA create insignificant polarization in PANI which has weakly affected the nuclear oscillations and resulted in increase in Raman intensity and gradually with the increase of DBSA the Raman intensity increases [4]. However, the lower intensity of Raman is contributed from collapse chains of PANI for excessive concentrations of DBSA (probably above 1.65 mmol). The collapse chains of PANI molecule effect the molecular orientation thus lead to the lower polarizability. This can be explained that during the polymerization, where the DBSA acts as "holder" to hold the aniline monomer to be micelles in aqueous medium. The more DBSA molecules present in the medium, the larger micelles are formed. The large micelles will captures more aniline monomers, hence during oxidative polymerization, PANI molecules may become longer chains. Thus, chains are bounced back and loose the repetition of molecular orientation which follows the polymer chains theory [19].
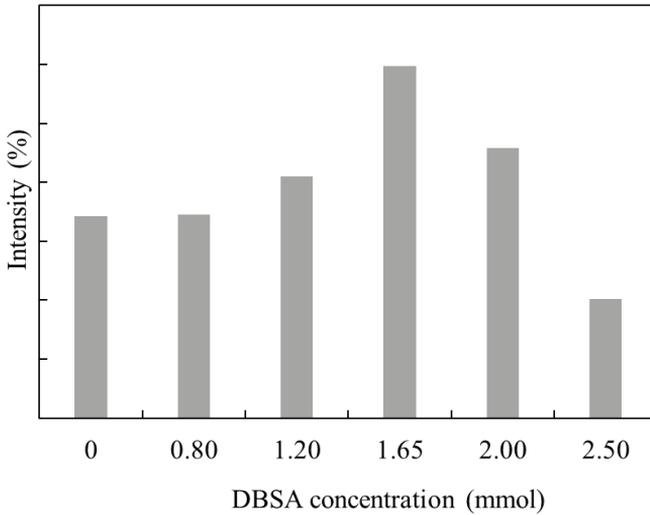
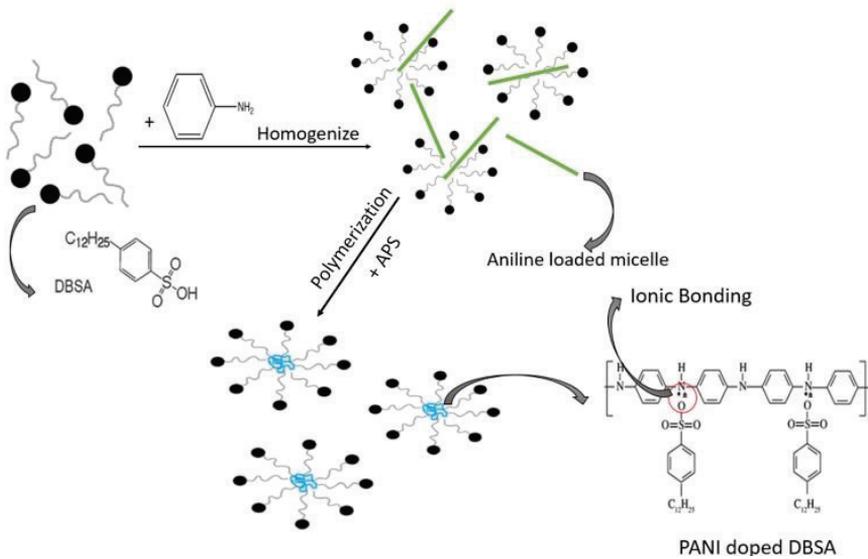Figure 4: Intensity of Raman Spectra of pristine PANI, PANI doped with 0.8, 1.65, 2.0 and 2.5 mmol DBSA

Figure 5: Reaction mechanism of doped PANI

3.3 SEM Characterization

PANI may develop in the form of wire, tubes, and particles while being doped. As shown in Figure 6(a), the pristine PANI may present in the globular form and the cluster of globular particles may result from agglomeration of particles. The synthesis PANI doped with DBSA shows the change in morphology of PANI particles compare to

undoped PANI by showing lesser clustering which may help to decrease the agglomeration effect. From. The suitable amount of DBSA produces small size of micelles that captures adequate amount of aniline monomers. It is resulted to the small size of PANI particles form. It can be seen in Figure 6(b) and 6(c), after being doped with DBSA at 0.8 and 1.65 mmol, the particle size has reduced and dispersed more. However, when the concentration of DBSA is increased to 2.0 (Figure 6(d)) and 2.5 mmol (Figure 6(e)), the PANI cannot stand after certain length of the chain [19-20] thus, the collapse of polymer chains occur. When collapse of polymer chains occurred, the molecular orientation is disturbed and resulted to agglomeration and larger size of PANI particles are formed.
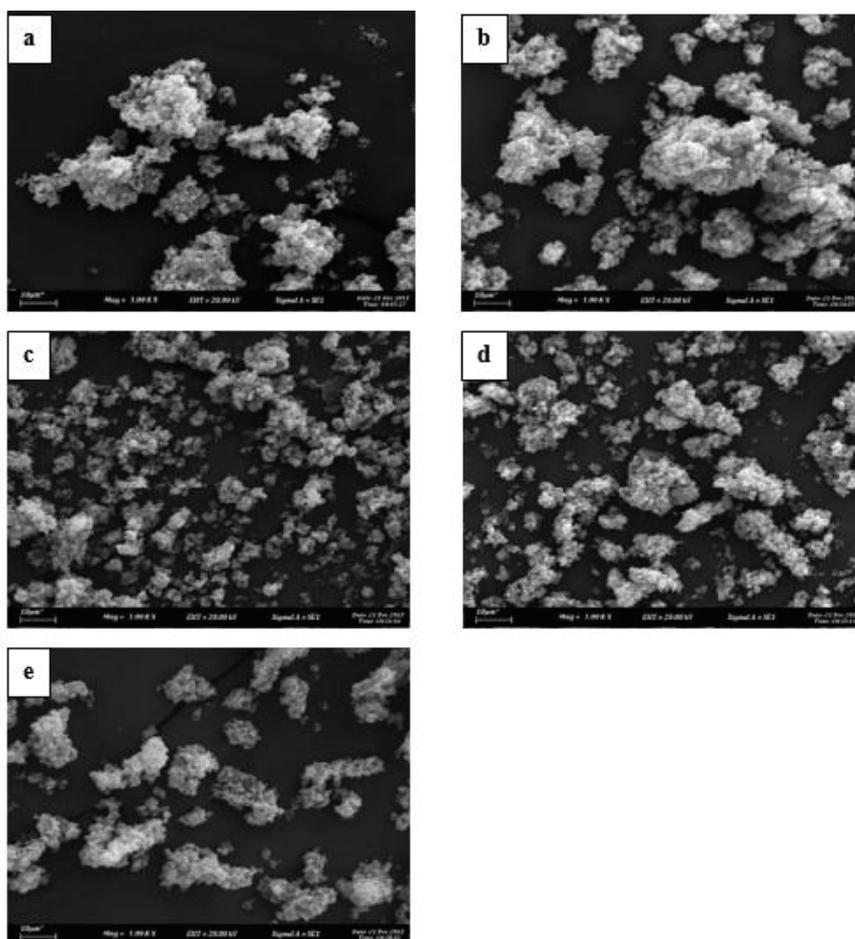

Figure 6: (a) Pristine PANI, (b) PANI with 0.8 mmol DBSA,
(c) PANI with 1.65 mmol DBSA, (d) PANI with 2.0 mmol DBSA and
(e) PANI with 2.5 mmol DBSA

4.0   CONCLUSION

The concentration of the DBSA affect the synthesis of PANI and hence promote the crystallinity region in DBSA doped PANI molecules. High tendency of aggregation of PANI particles during sample preparation yields irregularly size particles. Aggregated clusters of PANI-DBSA particles are semicrystalline in nature and the crystallinity increases with increasing feed concentrations of DBSA. It shows the PANI-DBSA powder has a good dispersion result as the percentage crystallinity increases up to certain concentration of DBSA. Above that concentration, DBSA also act as surfactant, where the polymer chains length becomes too long and it may tend to collapse. Therefore, excess DBSA molecule promote collapse in polymer chains and lower the crystallinity resulted from molecular orientation.

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