

Short Communication

Effect of Modified Nano Silica on the Conductivity and Morphology Characteristics of Oxalic Acid-Doped Polyaniline Composites

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Oxalic acid-doped polyaniline (OA-PANI) was incorporated with nano silica and amino silane-modified nano silica. The polymerization of aniline to produce OA-PANI incorporating nano silica (OA-PANI-NS) and PANI incorporating 3-amino-propyltriethoxysilane modified nano silica (OA-PANI-NS-AS) were carried out in 0.1 M oxalic acid in the presence of ammonium persulphate as an oxidizing agent. Different amounts of nano silica and 3-amino-propyltriethoxysilane modified nano silica (13%, 15%, 20%, 30% and 50% w/w) were incorporated with OA-PANI to investigate its conductivity behavior using an impedance test. The successful formations of OA-PANI-NS and OA-PANI-NS-AS were confirmed by FTIR. The morphology of OA-PANI-NS and OA-PANI-NS-AS were studied using XRD and FESEM. Based on the results, the conductivity of OA-PANI-NS and OA-PANI-NS-AS increased linearly with the increased amount of nano silica and 3-amino-propyltriethoxysilane-modified nano silica w/w%, from 13 to 20% w/w. Further increased in the amount of both fillers caused a significant decrease in the conductivity of OA-PANI-NS and OA-PANI-NS-AS. The maximum electrical conductivity achieved for OA-PANI-NS and OA-PANI-NS-AS were $1.43 \times 10^{-4} \text{ Scm}^{-1}$ and $4.0 \times 10^{-6} \text{ Scm}^{-1}$, respectively. Lower conductivity of OA-PANI-NS-AS compared to OA-PANI-NS due to the presence of 3-amino-propyltriethoxysilane inhibited the ion movement in the OA-PANI matrix caused by the agglomeration phenomenon.

Keyword: polyaniline composite, nano silica, modified nano silica, conductivity, morphology.

1. INTRODUCTION

Conductive polymers are still an emerging area. Some intrinsically conductive polymers are polyamide, polyvinyl alcohol, and polyaniline. Amongst these conductive polymers, polyaniline has

attracted a lot of attention due to its good environmental, chemical, and thermal stability. There are many studies discussed on the use of individual polyaniline, or polyaniline blended with other polymers or incorporated with fillers [1,2,3]. Conductive polymers such as polyaniline are gaining more and more importance due to their benefits in applications where flexibility, low weight, and conductivity are required, but these polymers are high in cost and hazardous.

The conduction property of polyaniline is very critical as it affects the performance of polyaniline. Polyaniline in doped form is more conductive due to the protonation that occurs at the imine groups, which causes delocalization of electrons at the polyaniline structure. The addition of filler such nano silica previously has been proven to enhance the conductivity of the polyaniline composite [4,5]. Johan [6] reported that the increment of conductivity was due to the morphology changes of the polyaniline composites structure as the structure became more amorphous with the addition fillers. The amorphous nature of the polyaniline composite improves the ions movements in the polyaniline structure which affects the conductivity.

Fillers play important roles to improve the mechanical, thermal, electric conductivity, and corrosion properties of the polymer. The physical characteristics of fillers also influence the polymer properties. For example, the replacement of polar groups on the surface of nano particles with the organic groups of silane may change the properties of polyaniline composite. A silane compound is used to modify nano particles. Surface modification of nano particles with a silane coupling agent will enhance their compatibility with the polymeric coating and prevent their agglomeration [7]. Rostami [8] investigated the mechanical properties nano silica loaded polyurethane as well as amino silane (aminopropyltrimethoxysilane) treated nano silica loaded polyurethane. They discovered that treated nano silica loaded polyurethane revealed better mechanical properties compared to untreated nano silica loaded polyurethane.

Thus, in the present study, polyaniline incorporated with nano silica (OA-PANI-NS) and polyaniline incorporated with 3-amino-propyltriethoxysilane modified nano silica (OA-PANI-NS-AS) were prepared in the presence of oxalic acid as dopant. The aim of this study is to determine the effect of incorporation nano silica and 3-amino-propyltriethoxysilane modified nano silica or fillers on the conductivity and the morphology of polyaniline composite.

2. MATERIALS AND METHOD

2.1 Sample preparation:

A 3-amino-propyltriethoxysilane-modified nano silica was prepared according to Dong [9]. First, 1 g of nano silica was heated at 140 °C for 2 h. Secondly, 1 mL of 3-amino-propyltriethoxysilane was added into fillers. Subsequently, 50 mL ethanol was added, and the mixture was stirred at 78 °C for 2 h. Finally, the fillers were heated at 200 °C for 1 h.

Polyaniline composite was chemically synthesized as described by Li [10] using 0.13 mL aniline as a monomer. The synthesis was conducted in oxalic acid solution (50 mL, 0.1 M). Different weight ratios of 3-amino-propyltriethoxysilane-modified nano silica (13%, 15%, 20%, 30% and 50% w/w) were

added into the solution. The mixture was stirred and sonicated for 1 h to make sure that the nano silica fillers and the monomer were well-mixed. Next, the mixture was cooled and stirred vigorously for 2 h at 0 °C. Pre-chilled ammonium persulphate (1.01 g in 100 mL) was added into the solution and the mixture was stirred at 0 °C for another 6 h. The reaction was left overnight for complete polymerization. On the next day, the mixture was centrifuged and the green solid precipitate was filtered and dried in the oven at 120 °C for 6 h. OA-PANI added with different ratios (13%, 15%, 20%, 30%, and 50% w/w) of nano silica (OA-PANI-NS) as well as polyaniline without the fillers (OA-PANI) were prepared according to the similar procedure as described above.

2.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) analysis was conducted to determine the structure and the possible interaction between polyaniline and fillers (3-amino-propyltriethoxysilane-modified nano silica and nano silica). The analysis was performed using potassium bromide (KBr) pellets. The FTIR spectra were recorded at the frequency range of 400 cm⁻¹ to 4000 cm⁻¹ with 4 cm⁻¹ resolutions.

2.3 X-ray diffraction

X-ray diffraction (XRD) was conducted to determine the effect of incorporating the fillers on the morphology structure of polyaniline. The analysis was performed at room temperature (25 °C). The samples were scanned at the range 10° ≤ 2θ ≤ 70°.

2.4 Conductivity

OA-PANI-NS and OA-PANI-NS-AS films were prepared according to Wang [11]. OA-PANI, OA-PANI-NS, and OA-PANI-NS-AS were coated on both sides of filter paper. The thickness of each film was measured using a thickness gauge. The overall thickness was ~0.21 mm.

For measurement of conductivity using Gamry instrument, impedance was done by sandwiching the films between two stainless steel electrodes of diameter 0.9 cm. The impedance was measured from 100 MHz to 1 Hz using sinusoidal wave of 10 mV. The conductivity of all samples was determined using the bulk resistance (R_b) value from the Nyquist plot. The conductivity (σ) was calculated according to Equation 1 [12]:

$$\sigma = \frac{d}{AR_b} \text{ Equation 1}$$

Where d is the sample thickness, A is the cross-section area of the sample and R_b is the bulk resistance.

2.5 FESEM

FESEM images of all samples were recorded to examine the surface morphology and structure of the samples. FESEM analysis was carried out using HITACHI S4500 (Tokyo, Japan) with EDAX software Genesis at Quasi-S at the required 50000X magnification with electron beam voltage 15 kV at room temperature. The sample was deposited on brass hold and sputtered with a thin layer of gold under vacuum.

3. RESULTS AND DISCUSSION

3.1 FTIR

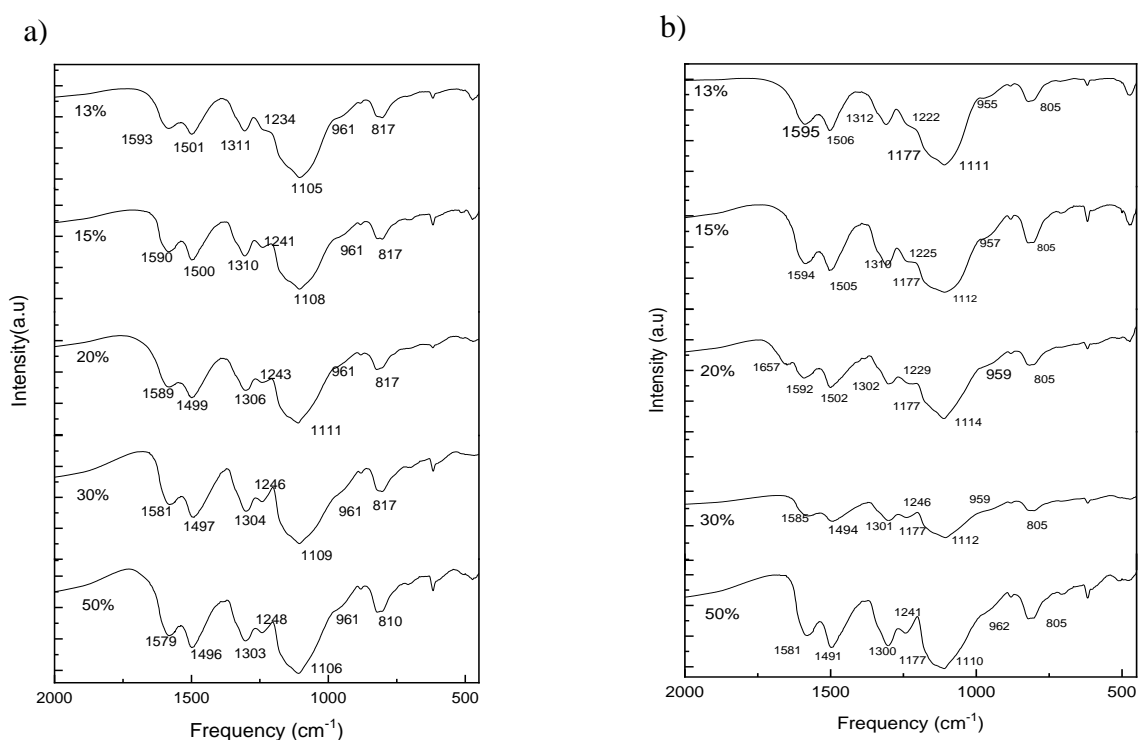


Figure 1. FTIR spectrum for a) OA-PANI-NS-AS with different weight of 3- amino-propyltriethoxysilane modified nano silica (50% w/w, 30% w/w, 20% w/w, 15% w/w and 12% w/w) and b) OA-PANI-NS with different weight nano silica (50% w/w, 30% w/w, 20% w/w, 15% w/w and 13% w/w)

The interaction between OA-PANI and fillers were investigated by using the FTIR analysis. Figure 1(a) exhibits FTIR spectra of OA-PANI-NS-AS while Figure 1(b) shows OA-PANI-NS. The interaction was determined based on the shifting of characteristic peaks at the region 1225 cm^{-1} to 1247 cm^{-1} , which corresponded to $\nu(\text{C-OH})$ of oxalic acid. When 20 w/w% of 3- amino-propyltriethoxysilane modified nano silica was added, the peak shifted to a lower frequency of 1240 cm^{-1} . The shifting of this peak was correlated to the hydrogen bonding of N-H presented in the OA-PANI-NS-AS. The N of OA-

PANI-NS-AS formed hydrogen bonding with H of oxalic acid (Figure 2). The low downshifted value was hypothesized to be attributed to N-H hydrogen bonding.

In Figure 1(b), the $\nu(\text{C-OH})$ peak of oxalic acid has downshifted from 1247 cm^{-1} to 1229 cm^{-1} for 20 w/w% of nano silica fillers. The significance shifting indicated that the formation of strong hydrogen bond (O-H) between hydrogen atoms, H to electronegative oxygen atoms, O in polyaniline and nano silica. This observation suggested that the nano silica fillers had permeated into OA-PANI to form hydrogen bond, which occurred at the oxalic acid side instead of at polyaniline backbone (Figure 3). Similar observation on large decreased of the FTIR frequency shifting caused by O-H bond in a previous study [13]. Cross and Jones [14] claimed that the downshifted value of N-H bond was lower than the downshifted value of O-H bond.

The FTIR spectra also presented the effect of the fillers addition on the electronic distribution around N atom in the OA-PANI structure. The FTIR band at 1106 cm^{-1} denoted the conductivity of behavior of polyaniline. High intensity reflects high electronic distribution around the N atom which caused high conductivity. Based on the result, OA-PANI added with 20% w/w of fillers was suggested to have a better electronic distribution compared to other OA-PANI composite samples.

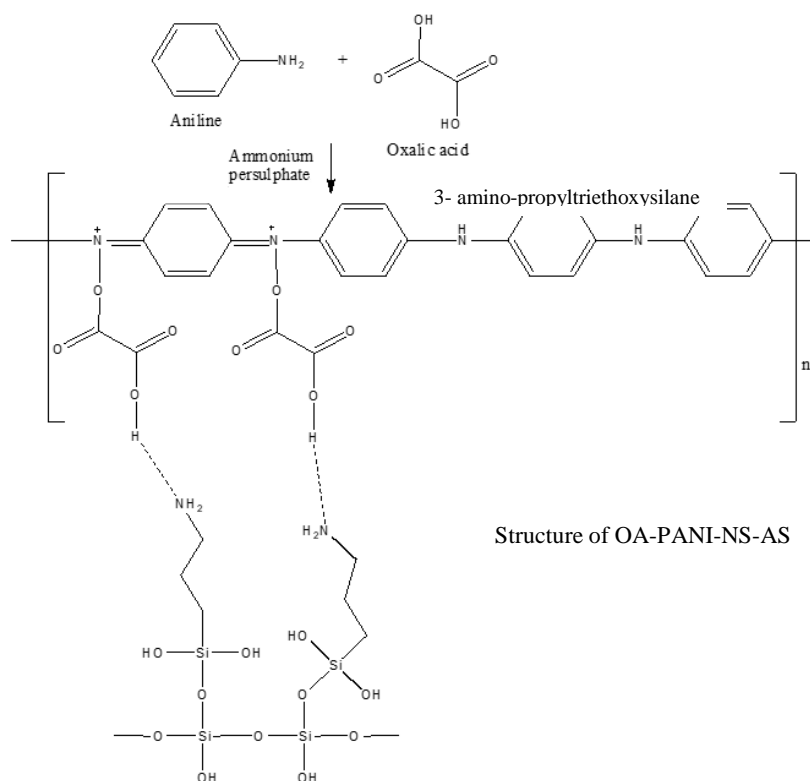


Figure 2. Structure of OA-PANI-NS-AS

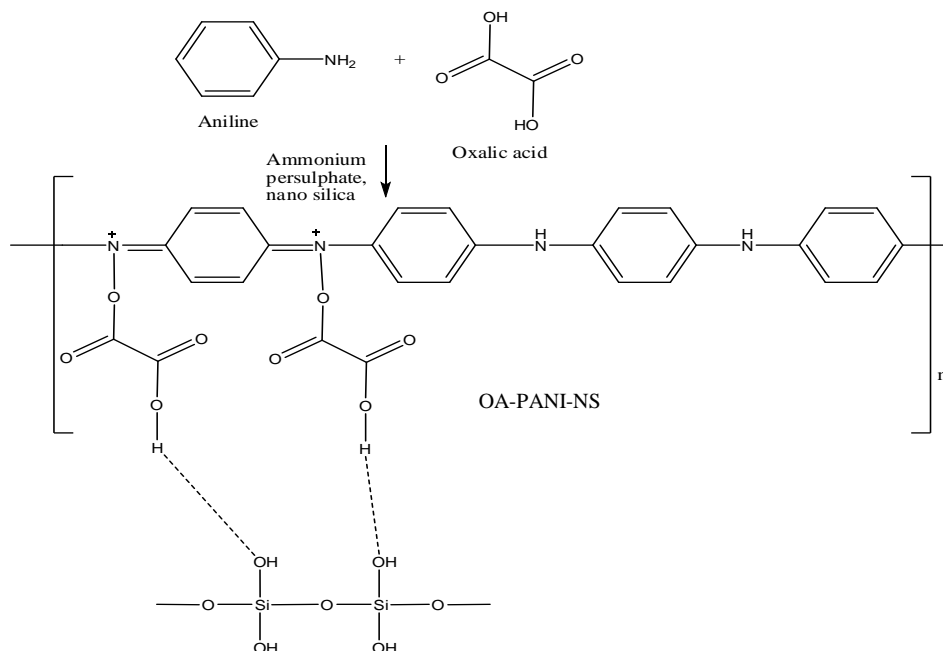


Figure 3. Structure of OA-PANI-NS

3.2 Conductivity

The conductivity of OA-PANI with different weight ratios (10%, 15%, 20%, 30%, and 50% w/w) of 3-amino-propyltriethoxysilane-modified nano silica (OA-PANI-NS-AS) and nano silica (OA-PANI-NS) fillers were conducted to determine the optimum conductivity value, which was calculated from the impedance plot. The conductivity versus different weight ratios of 3-amino-propyltriethoxysilane-modified nano silica is shown in Figure 4(a), while the conductivity versus different weight ratios of nano silica is shown in Figure 4(b).

The conductivity increased with an increase in weight of nano silica from 10 to 20% w/w. In Figure 4(a), the maximum conductivity was found at 20% w/w of OA-PANI-NS-AS with the conductivity value of $4.0 \times 10^{-6} \text{ S cm}^{-1}$. However, the conductivity decreased significantly from 20% w/w to 30% w/w, with a small increase at 50% w/w. A similar curve pattern was observed in Figure 4(b). The highest value was observed to be $1.43 \times 10^{-4} \text{ S cm}^{-1}$ obtained with 20% w/w of OA-PANI-NS. Both samples achieved maximum conductivity value at 20% w/w of nano silica, which could relate to the electronic distribution as well as the morphology changes. The addition of fillers has also affected the electronic distribution around N atom in OA-PANI structure as discussed previously in the FTIR section. Based on the results, OA-PANI-NS showed higher conductivity value compared to OA-PANI-NS-AS due to the presence of amino silane on nano silica surface of OA-PANI-NS-AS, which inhibited the movement of ions in polyaniline structure.

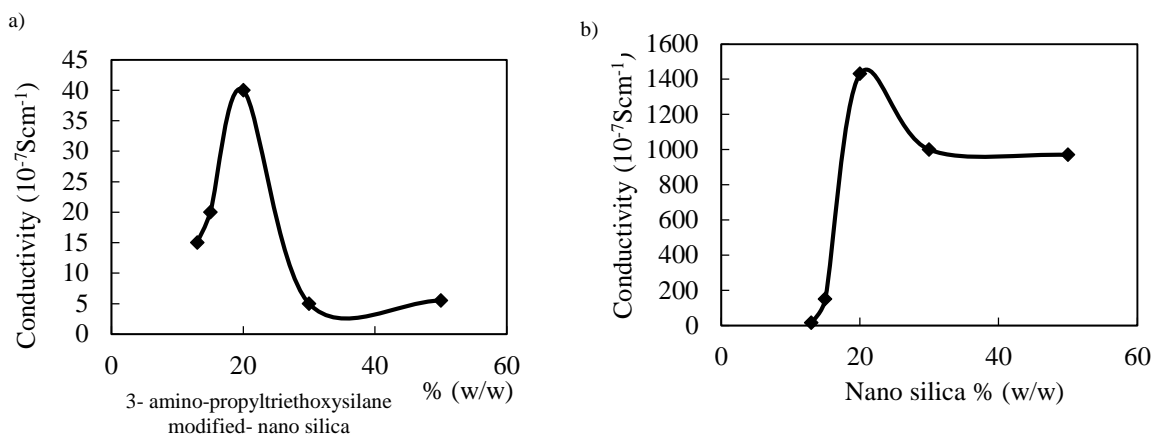


Figure 4. The effect of different weight ratios of 3-amino-propyltriethoxysilane -modified nano silica and nano silica (50% w/w 30% w/w, 20% w/w , 15% w/w and 12% w/w) on the conductivity of a) OA-PANI-NS-AS and b) OA-PANI-NS, respectively. The analysis was conducted at room temperature.

3.3 XRD

XRD was conducted to determine how fillers affected the semi-crystalline structure of the polyaniline films. Figure 5(a) and 5(b) show the X-ray diffraction patterns for OA-PANI-NS-AS and OA-PANI-NS, respectively. The patterns were recorded at 2θ .

Based on the patterns of 3(a), 3(b), 4(a), and 4(b), two peaks could be observed at $2\theta = 21^\circ$ and 25.5° which attributed to the periodic vertical parallel structure in the main chain of polyaniline [15,16]. The characteristic peaks of OA-PANI in the presence of fillers become less prominent and broadened upon fillers affirming the decrease of the crystalline phase and its predominantly amorphous nature. For patterns 5(a) and 5(b), OA-PANI with 20% w/w fillers content was observed to be more amorphous compared to other samples. Above 20% w/w of fillers content, a more prominent peak was observed suggesting growth in the degree of crystallinity. The growth was due to high viscosity of fillers upon the introduction of more fillers in the polyaniline composite structure [17]. The variation in the degree of crystallinity values was correlated to the morphology changes of OA-PANI when fillers were added [6]. Similar XRD diffraction patterns were reported in previous research [17].

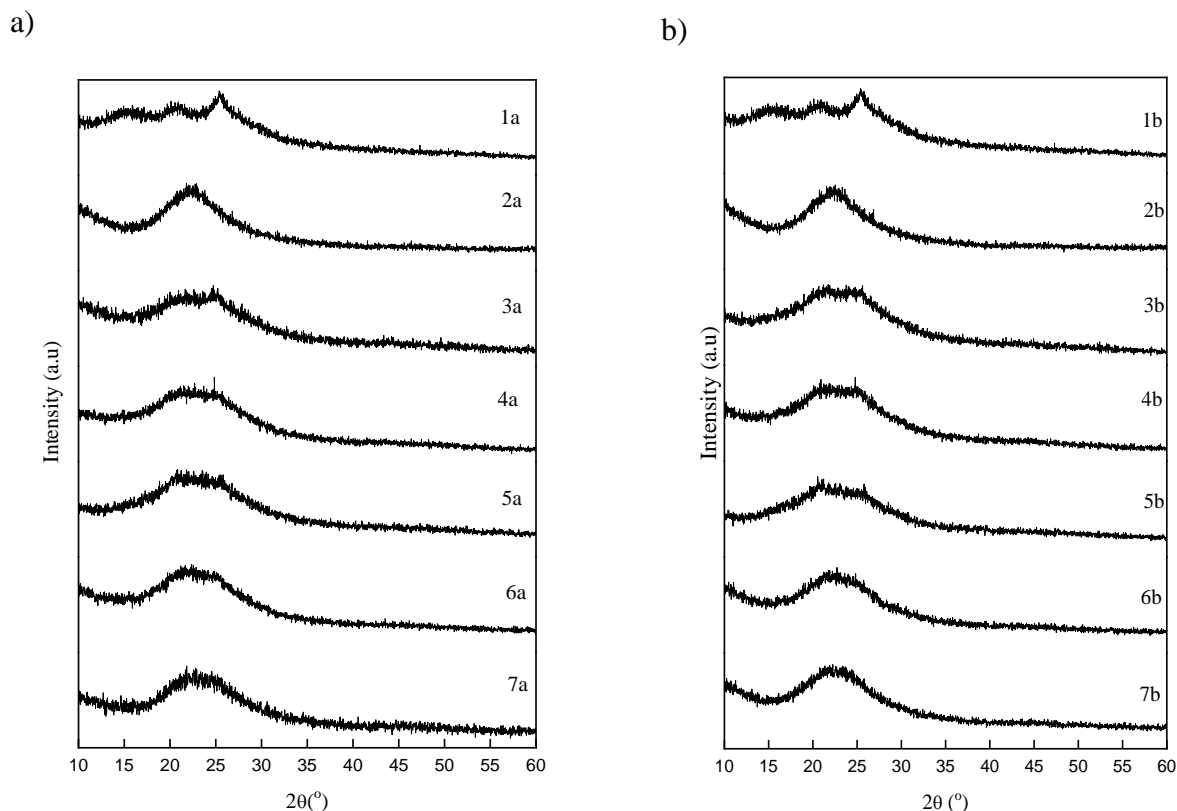


Figure 5. X-ray diffraction patterns of (a) OA-PANI-NS-AS, 1a: OA-PANI, 2a: 3-amino-propyltriethoxysilane-modified nano silica, 3a: 13% w/w, 4a: 15% w/w, 5a: 20% w/w, 6a: 30% w/w, 7a: 50% w/w of 3-amino-propyltriethoxysilane- modified nano silica; (b) OA-PANI-NS, 1b: OA-PANI, 2b: nano silica, 3b: 13% w/w, 4b: 15% w/w, 5b: 20% w/w, 6b: 30% w/w, 7b: 50% w/w of nano silica.

The amorphous nature of the materials could also enhance their conductivity. The variation in conductivity observed upon the addition of fillers in OA-PANI was attributed to the amorphous nature of the material. Hence, it could be implied that OA-PANI-NS containing 20% w/w nano silica was more amorphous compared to OA-PANI-NS-AS containing 20% w/w of 3-amino-propyltriethoxysilane-modified nano silica, which exhibited the highest conductivity value.

3.4 FESEM

FESEM was conducted to observe the surface morphology of polyaniline, OA-PANI-NS, and OA-PANI-NS-AS. Figure 6(a) displays the surface morphology of polyaniline which possessed a tubular structure. Upon addition of 20% w/w of nano silica fillers, the surface morphology of OA-PANI-NS became a coral-like structure as shown in Figure 6(b). Based on this figure, the nano silica fillers were uniformly dispersed on the tubular structure of polyaniline. The morphology image of OA-PANI-NS-AS silica is represented in Figure 6(c) which shows the tubular structure aggregated with spherical shape. The aggregation of the modified nano fillers occurred at the end of the tubular structure, which might due to the non-uniform dispersion of 3-amino-propyltriethoxysilane modified nano silica fillers in the

polyaniline structure. Naguib [18] suggested that surface modification of nanoparticles with silane would enhance their compatibility with the polymeric coating and prevent agglomeration. However, a contradict result was shown as the 3-amino-propyltriethoxysilane modified nano silica formed agglomeration on the polyaniline matrix. The non-uniform dispersion of 3-amino-propyltriethoxysilane modified nano silica fillers might be due to the high hydrophilic environment of silica in the OA-PANI-NS-AS structure and the large size of the silane compound [19]. The two factors caused a steric effect which reduced the miscibility and dispersity of 3-amino-propyltriethoxysilane modified nano silica as well as the conductivity value of OA-PANI-NS-AS compared to OA-PANI-NS.

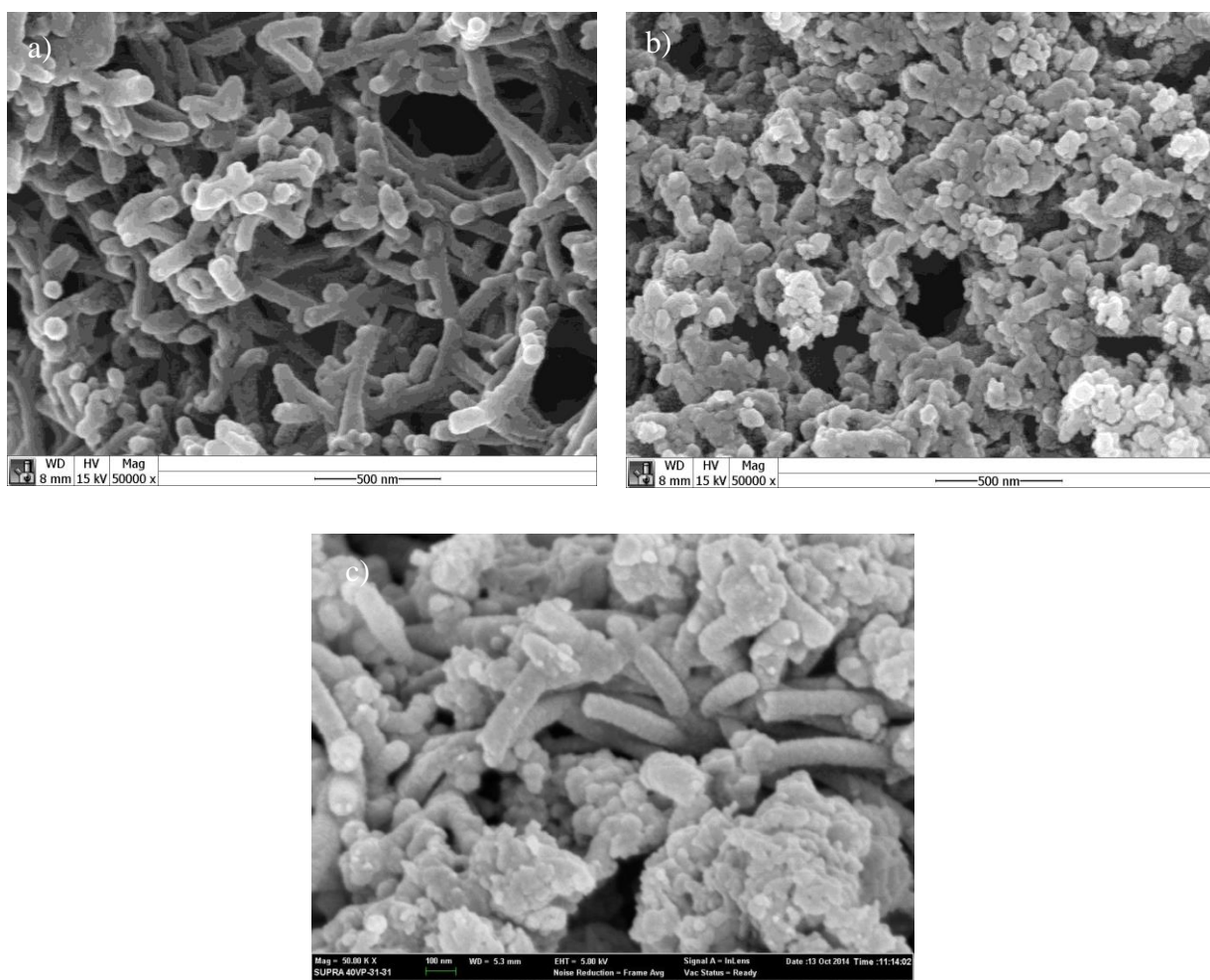


Figure 6. FESEM images of (a) OA-PANI, (b) OA-PANI-NS and (c) OA-PANI-NS-AS at 50 000 X

4. CONCLUSION

Polyaniline added with different concentrations of amino-silane-modified nano silica fillers were successfully synthesized and characterized. Infrared spectroscopy data suggested that the increase in the conductivity upon addition of 20 w/w% of nano silica was due to the electronic distribution at N atom

in polyaniline structure. XRD results indicated that amino silane-modified nano silica fillers concentration affects the morphology of polyaniline. The addition of amino silane-modified nano silica fillers had reduced the semi-amorphous nature of polyaniline. Impedance measurements revealed that amino silane-modified nano silica fillers concentration affects the conductivity of polyaniline with the highest conductivity observed at 20w/w% of fillers. FESEM showed that OA-PANI-NS-AS revealed lower conductivity value compared to OA-PANI-NS due to the presence of 3-amino-propyltriethoxysilane modified nano silica fillers inhibit the ion movement in the PANI matrix. It is believed this phenomenon is caused by the agglomeration of 3-amino-propyltriethoxysilane modified nano silica in the OA-PANI matrix.

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