Journal of Physical Science, Vol. 21(2), 81–97, 2010

Conductive Polymer Based on Polyaniline-Eggshell Powder (PANI-ESP) Composites

Supri A. Ghani* and Heah Chong Young

School of Materials Engineering, University Malaysia Perlis,
02600 Jejawi, Perlis, Malaysia

*Corresponding author: supri@unimap.edu.my

Abstract: *In this study, we analysed the characteristics of eggshell powder (ESP)-filled polyaniline (PANI) composites. Raw material eggshells were dried in an oven and blended into a powder. 1-methyl-2-pyrrolidinone was added to PANI powder to produce a PANI solution, and activated charcoal powder was then added. The solution was placed into a heating mantle with a controlled temperature until a uniform solution was produced. The resultant conductive polymer was then analysed by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Brunauer, Emmett and Teller (BET) and X-ray diffraction (XRD). The results of these analyses show that PANI-ESP did not undergo a chemical structural change. The only interaction that occurred was between the filler reinforced with carbon black (CB) and the matrix. The structure of the composite was a face centred cubic (FCC) structure with an average lattice parameter of 0.72 nm. The surface morphology of the composites shows that agglomeration occurred to complete the connection of the conductive path, thus improving the conductivity behaviour. The conductivity of the PANI-ESP composite was also studied and measured in situ during the mixing process.*

Keywords: conductive polymer, eggshell powder, polyaniline

Abstrak: *Sifat-sifat komposit polianilina (PANI) diisi serbuk kulit telur (ESP) telah dikaji. Bahan mentah iaitu kulit telur telah dikeringkan di dalam ketuhar dan dikisar sehingga menjadi serbuk. 1-metil-2-pyrrolidinone ditambah ke dalam serbuk PANI untuk menghasilkan larutan PANI dan seterusnya serbuk arang yang diaktifkan ditambah. Larutan tersebut diletakkan dalam mantel pemanasan dengan suhu terkawal sehingga larutan yang sekata dihasilkan. Polimer konduksi yang terhasil dianalisa menggunakan scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Brunauer, Emmett and Teller (BET) dan X-ray diffraction (XRD). Keputusan analisa-analisa menunjukkan bahawa PANI-ESP tidak mengalami perubahan secara kimia. Hanya terdapat interaksi antara pengisi dan penguat karbon hitam (CB) dengan matriks. Struktur komposit ini ialah struktur padu face centred cubic (FCC) dengan purata jarak antara partikel sebanyak 0.72 nm. Morfologi permukaan komposit menunjukkan bahawa pengaglomeratan telah berlaku untuk melengkapkan sambungan bagi laluan konduksian. Kekonduksian bagi komposit PANI-ESP juga telah dikaji dan diukur in situ semasa proses.*

Kata kunci: polimer konduksi, serbuk kulit telur, polianilina

1. INTRODUCTION

The ability of polymers to become electrically conductive was shown when a scientific breakthrough demonstrated that to become electrically conductive, a polymer must imitate a metal, which means that electrons in polymers must be free to move and must not be bound to atoms. Most polymeric materials are poor conductors of electricity because a large number of free electrons are not available to participate in the conduction process.[1] In principle, an oxidation or reduction reaction is often accompanied by the addition or removal of electrons. Therefore, a polymer might become electrically conductive by removing electrons, a process described as doping.[2] Doping means increase in carriers in conjugated polymers where this process involves electron acceptors and electron donors, respectively. This unexpected discovery did not only challenge the traditional concept that organic polymers are only insulators, but also established a new class of conducting polymers called ‘synthetic metals’.[3,4]

Since the discovery of electrical conductivity in ionic polymers, various ionically conducting polymers or polymer electrolytes have been prepared for a wide range of applications. The most interesting property of conducting polymers is their high (almost metallic) conductivity, which can be altered by simple oxidation or reduction and also by bringing the material into contact with different compounds.

The first and most widely used conducting polymeric systems were composites in which an insulating polymer matrix was filled with a particulate or fibrous conductive filler, such as a carbon or metal, to impart high conductivity. Applications for such composites are widespread; these composites are used for interconnections, printed circuit boards, encapsulations, die attach, heat sinks, conducting adhesives, electro-magnetic interference (EMI) shielding, electrostatic discharge (ESD) and aerospace engineering.[5,6] Unfortunately, these conductive fillers will impart heavy weight, poor surface finish, poor mechanical properties and easy oxidative degradation to the end product.

Polyaniline (PANI) is a promising conducting polymer due to its easy synthesis, environmental stability and high electrical conductivity. The preparation of PANI composites with various materials has received great attention because of their unique properties and applications in various electrical devices. However, the main problem associated with the effective utilisation of all intrinsically conducting polymers (ICPs), including PANI, is inherent in their lower level of conductivity compared to metal and their infusibility and poor solubility in all available solvents.[5] Polymer composites containing PANI (matrixes) have received much attention because of the resultant combination of improved processability and fairly good mechanical properties coupled with good conductivity.

Many studies related to PANI or eggshell powder [ESP ($CaCO_3$)] currently exist. Research on creating blends of PANI with conventional polymers concluded that these blends possess relatively high conductivity with good mechanical properties.[6] PANI/polyamide blended films have been successfully prepared, and their excellent electrical and mechanical properties have contributed to the film industry.[4] In addition to this work, the preparation and characterisation of PANI materials with ferromagnetic properties has also been primarily performed.[4] Although the first goal of their studies was to fabricate composites with good room temperature conductivity, only low values of conductivity of 10^{-6}–10^{-3} S/cm were obtained.[7]

Because PANI is one of the most promising conducting polymers with enhanced properties, prodigious research papers are available concerning the synthesis and application of PANI composites.[8] Many papers dealing with the preparation of conducting composites of PANI, such as TiO_2/PANI[9], ZrO_2/PANI, Fe_3O_4/PANI, zeolite/PANI, MoO_3/PANI, MnO_2/PANI, WO_3/PANI and others, have been published.[10]

Another area of research exists that is based on $CaCO_3$, for example, the correlation between hardness and yield stress of $CaCO_3$ filled polyethylene.[11] The evaluation of $CaCO_3$ dispersion in polypropylene composite fibres shows that: 1) Fourier transform infrared (FTIR) spectroscopy may be reliably applied for the evaluation of the relative degree of dispersion of calcite in composites,[12] 2) the impact strength of high density polyethylene (HDPE) is increased upon $CaCO_3$ reinforcement[13] and 3) the presence of the filler influences the crystallisation process and leads to an increase of the amount of imperfect crystalline phase.[14] Other results indicated that $CaCO_3$ nanoparticles could induce nucleation but slow the mobility of polymer chains.[15]

However, to the best of our knowledge, nothing has been reported on the preparation of PANI/eggshell composites. In this project, PANI is used as a matrix polymer in which eggshells act as a filler that is added to the composites.

2. EXPERIMENTAL

2.1 Materials

PANI (emeraldine base) with an approximate Mw of 5000 was obtained from Sigma-Aldrich. 1-methyl-2-pyrrolidinone with a Mw of 99.13 was supplied by AR Alatan, Alor Star, Kedah, Malaysia. Eggshells were obtained from a Perlis local market, and activated charcoal powder was supplied by Mega Makmur Sdn. Bhd., Pulau Pinang, Malaysia.

2.2 Sample Preparation

First, raw material eggshells were washed and dried in an oven to eliminate contaminants and odour. Then, the eggshells were blended into a powder in a blender. The powder was then sieved using an industrial sieve to obtain the required particle size of 63 µm. This ESP was then used in further experiments.

2.3 Mixing and Compounding

1-methyl-2-pyrrolidinone (10.33 g) was added to 0.25 g of emeraldine base PANI and mixed to produce a PANI solution. Activated charcoal powder (0.50 g) was then added to the solution, and the solution was aliquoted in equal volumes into five test tubes. Five different amounts of eggshell filler (0.25 g, 0.50 g, 0.75 g, 1.00 g and 1.25 g) were added into the solution in the test tubes, respectively. Table 1 shows the composition of the mixture for the PANI-carbon black (CB) composite. Table 2 shows the composition of the mixture for the PANI-CB-eggshells composite. The weight percentage of ESP and the molarity of PANI-N-methyl pyrrolidinone (PANI-NMP) were calculated according to the following formulas:

$$\text{Weight \% of ESP} = \frac{ESP}{MA} \times 100\% \tag{1}$$

$$\text{Molarity of PANI-NMP} = \frac{VS}{Mw} \times 100\% \tag{2}$$

where *ESP* is the amount of ESP, *MA* is the amount of matrix, *Mw* is the Mw of the eggshells and *VS* is the volume of NMP solvent. The PANI solution (conductive polymer) was placed into a heating mantle with a controlled temperature of 100°C, which is the boiling point of the solution, for 30 minutes. The conductive polymer that was produced was analysed by scanning electron microscopy (SEM), FTIR and X-ray diffraction (XRD). After these analyses, an electrical conductivity test was performed by connecting a digital precision multimeter (AR Alatan, Alor Star, Kedah, Malaysia) to a printed circuit board (PCB) that was coated with the conductive polymer composites. Before the conductivity test, the PCBs were placed into a oven heated at 105°C for 30 minutes.

Table 1: Formulation of blend composition of PANI-ESP composites.

Blend composition	PANI (g)	ESP (g)	NMP (g)	CB (g)
PANI	0.25	0	10.33	0.5
PANI/ESP$_1$	0.25	0.25	10.33	0.5
PANI/ESP$_2$	0.25	0.50	10.33	0.5
PANI/ESP$_3$	0.25	0.75	10.33	0.5
PANI/ESP$_4$	0.25	1.00	10.33	0.5
PANI/ESP$_5$	0.25	1.25	10.33	0.5

Table 2: Molar concentration and weight percent of PANI-ESP composites.

PANI-1-methyl-2-pyrrolidinine (M)	CB (g)	ESP (g)	% wt of ESP
0.005	0.5	0	0
0.005	0.5	0.25	2.21
0.005	0.5	0.50	4.41
0.005	0.5	0.75	6.62
0.005	0.5	1.00	8.83
0.005	0.5	1.25	11.03

2.4 FTIR Spectroscopy

A small amount of potassium bromide (KBr) powder was placed into a mould, and the mould was pressed at 4 tons for 2 minutes in a cold press machine to produce a KBr pellet. The KBr pellet was then dipped into 1.25 g of ESP so that part of the gel-like sample was absorbed into the pellet. Because the ESP sample is in a gel-liked form, the sample preparation for FTIR followed the oil-based preparation method. Perkin Elmer FTIR Spectrum RX1 (Pulau Pinang, Malaysia) spectrometer was used for the analysis.

2.5 Scanning Electron Microscopy (SEM)

The control sample without ESP and experimental samples with ESP as filler (0.25 g and 0.75 g) were prepared for SEM. First, 0.8 ml of each sample was added to 0.4 ml of polyester and 0.2 ml of methyl ethyl ketone peroxide

(MEKP) (crosslinking agent) and stirred for 2 minutes to obtain a uniform solution. This purpose of this step is to make sure that the gel-like samples adhere to the PCB. After mixing, the samples were evenly coated onto 2 cm x 2 cm PCBs. The PCBs were placed in an oven and heated at 80°C for 5 hours to dry the samples. Finally, each board was cut into four equal portions. Only one of the portions, that had the best surface, was used for SEM morphology analysis. A scanning electron microscope (JEOL JSM 6460 LA, Perkin Elmer Sdn. Bhd., Kuala Lumpur) was used. Note that because the sample is conductive in nature, coating with an Auto Fine Coater is unnecessary.

2.6 X-ray Diffraction

Using XRD, we identified multiple phases and amorphous materials in partially crystalline mixtures of the conductive polymer. Samples were mixed well and used in XRD analysis. A XRD-6000 Shimadzu (Kuala Lumpur) X-ray diffractometer equipped with auto-search/match software for the qualitative analysis was used to produce a diffraction pattern of the crystalline solid.

2.7 Conductive Testing

The control sample without ESP and experimental samples with ESP as filler (0.25 g, 0.50 g, 0.75 g, 1.00 g and 1.25 g) were prepared for conductive testing. First, 0.8 ml of each sample was added to 0.4 ml of polyester and 0.2 ml of MEKP and stirred for 2 minutes to obtain a uniform solution. The purpose of this step is to make sure that the gel-like samples adhere to the sensing devices, which have connected wire. After mixing, the samples were evenly coated onto the sensing devices. The sensors were placed into an oven and heated at 80°C for 5 hours to dry the sample. After the samples were dried, the sensors were connected to a digital precision multimeter to measure the resistivity under a controlled temperature of 50°C in sealed beaker.

2.8 Conductive Testing Based on Application

A sensing test was performed using 40 ml of ethanol, 50 g of coffee powder and ammonia (NH_3) gas using the same sensing device to measure the conductive polymer response to the resulting smells under a controlled temperature of 50°C in a sealed beaker. Before this analysis, the sensing devices were heated in an oven at 105°C for 30 minutes.

2.9 Brunauer, Emmett and Teller (BET) Test

The conducting polymer material was heated and degassed by vacuum force or inert gas purging to remove adsorbed foreign molecules. A controlled inert gas, such as N_2, was introduced, and the gas was adsorbed or, alternatively, withdrawn and desorbed. The amount of gas molecules adsorbed or desorbed was determined by the variation in pressure due to the adsorption or desorption of the gas molecules by the material (the adsorbent). Various amounts of gas molecules are adsorbed or desorbed at different doses of the gas (the adsorbate). Knowledge of the area occupied by one adsorbate molecule and the use of an adsorption model allowed for the determination of the total surface area of the material.

3. RESULTS AND DISCUSSION

3.1 Brunauer, Emmett and Teller (BET) Analysis

The BET analyser showed that the surface area of the ESP was 43.7143 m^2/g, whereas the Langmuir surface area was 90.3459 m^2/g. The single point adsorption total pore volume of pores less than 66.2933 nm in width at $P/Po = 0.969929435$ was 0.078075 cm^3/g. The Barret, Joyner and Halenda (BJH) adsorption average pore width (4V/A) was 9.9164 nm, and the BJH desorption average pore width (4V/A) was 14.4322 nm. Traditionally, BET surface area measurements have been used to determine the specific surface area of colloidal inorganic oxides and polymer latexes.[16] As far as we are aware, there have been very few BET studies on conductive polymer-based materials. The surface area and porosity values obtained show that the application of ESP into a PANI matrix enhanced its composite properties because it created a different phase relative to the matrix materials. These are important characteristics that affect the quality and utility of the PANI-eggshell composite and are important in understanding its structure, formation and conductivity potential, which corresponded well to its applications in various fields.

As shown in Figure 1, we conclude that the relative pressure above 0.8 reflects a dramatic adsorption and desorption behaviour, meaning that above this point, the applied pressure is sufficient to allow the surface to be saturated by the adsorbate. Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure at a constant temperature.[17] The determination of specific surface by means of the BET theory is based upon the phenomenon of the physical adsorption of N_2 gases on the external and internal surfaces of a sample and is able to show the porosity and pore surface of the ESP, which is different in its physical properties from the matrix of conductive polymer. The amount of adsorbed gas is dependent on its relative vapour pressure and is proportional to the total external and internal surface of the material. The porous structure of ESP will be an added advantage for electron transfer when current is applied to the conductive polymer.

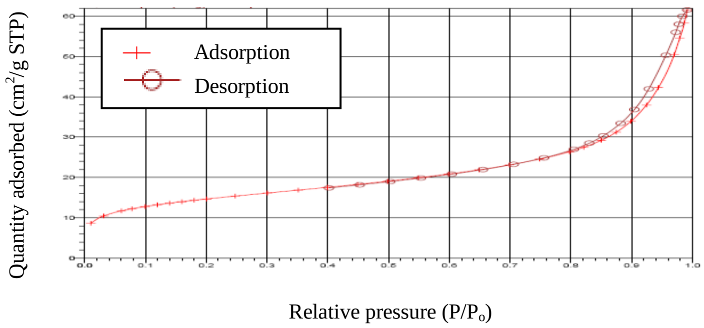


Figure 1: BET analysis shows quantity adsorbed versus relative pressure.

Figures 2 and 3 show the pore volume and pore area of the ESP. The pore volume and pore area decrease with increasing pore width. There are a few differences between BET and Langmuir surface area values, but the main difference is that Langmuir values can only be used for surfaces that are covered by one layer of gas and BET values are calculated using a multilayer model. The Langmuir adsorption isotherm was determined for single layer adsorption and gave a curve that describes the fraction of the surface area of the adsorbent covered with solute as a function of the concentration of the solute in the contacting liquid phase.

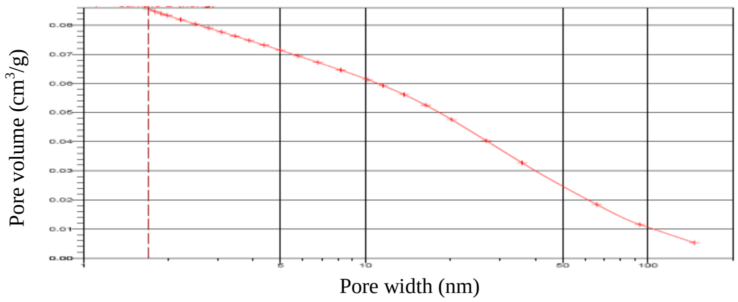


Figure 2: BET analysis shows the pore volume versus pore width.

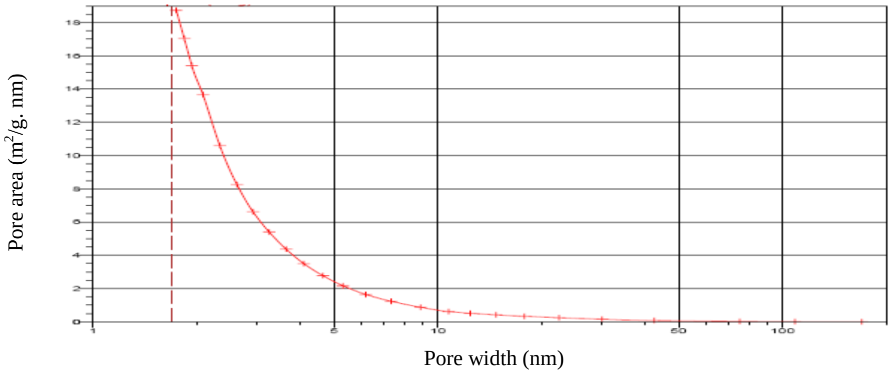


Figure 3: BET analysis shows pore area versus pore width.

3.2 FTIR Spectroscopy

The main goal of infrared (IR) spectroscopy analysis was to determine the chemical functional groups in the PANI-eggshell conducting polymer sample. Different functional groups absorb characteristic frequencies of IR radiation. From the result shown in Figure 4, high wavenumbers were observed that presented very strong spectrum absorption intensity peaks at 3525.01 cm^{-1} corresponding to the NH group. These peaks are perfectly positioned to correspond to an aromatic amine (NH_2). Because the peak intensity was 1658.22 cm^{-1}, this molecule must be a primary aromatic NH_2. Aromatic C=O bonds and C=C bonds also fall into this interval. The peak at 2910.16 cm^{-1} is within the range of C-H bonds and $-CH_2$ asymmetric bonds.

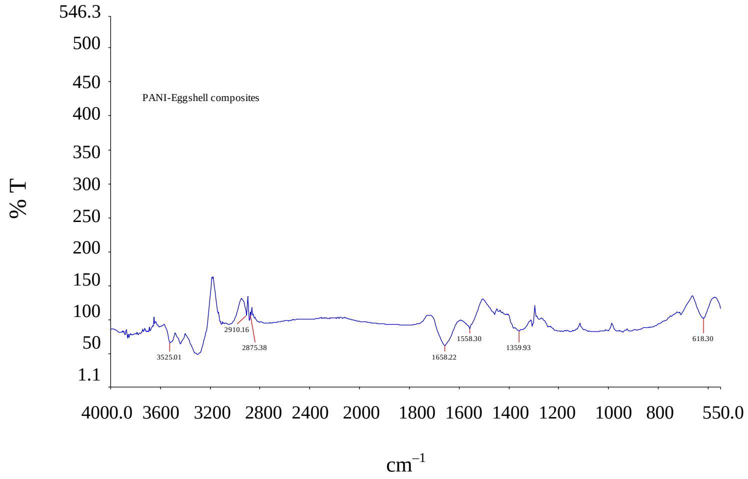


Figure 4**:** FTIR spectrum of conductive polymer based on PANI-ESP composites.

Small peaks located in the region between 600 and 700 cm^{-1} were also observed. The bands at 618.30 cm^{-1} can be assigned as a bend of a benzene ring. These bands confirm that the source of unsaturation is a benzene ring. Thus, it is a mono-substituted benzene ring. Because we know that we have a primary aromatic NH_2 and a mono-substituted benzene ring, the molecule must be aniline.[18] Because the aniline is not an individual substance in this composite, S-O bends and inorganic sulphates were found between 610 and 680 cm^{-1}.

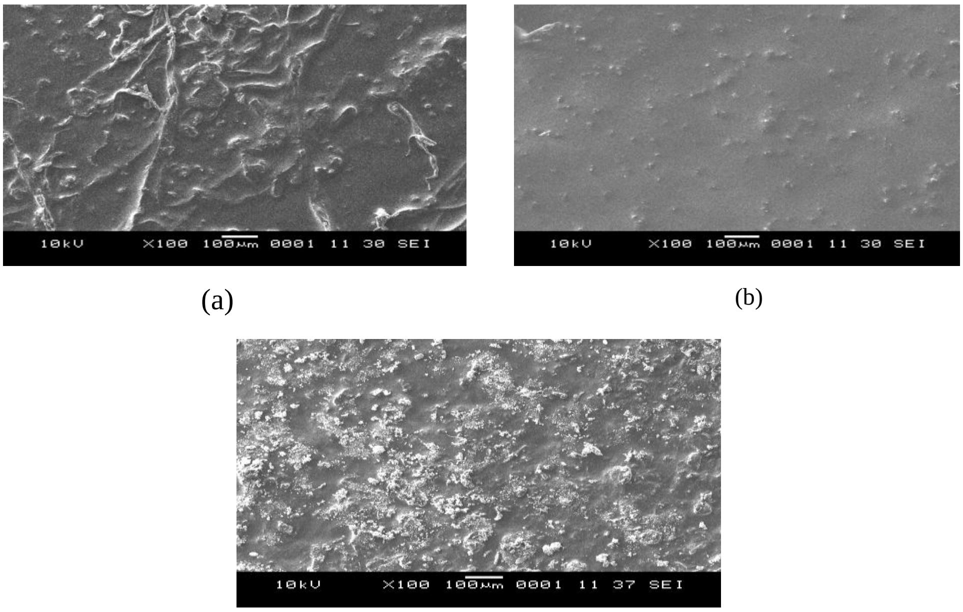
In addition, a peak at 2875.38 cm^{-1}, which falls in between 2835 and 2878 cm^{-1}, shows that the functional group of this conductive polymer structure contains a CH_3 symmetric and CH_2-O symmetric C-H strength. Moreover, additional peaks at 1558.30 and 1359.93 cm^{-1} indicate a N-H in-plane bend and the presence of N-O strength, respectively. From the results obtained, all expected functional groups were revealed, further confirming that the structure of the PANI-eggshell composite is exhibited in the composite. Functional groups play an important role in improving the thermal or conductivity properties of conductive composites.[10] In the PANI-ESP composites, no chemical change was found within the structure. The only interaction occurs between the filler and the reinforcement of CB with the matrix.

3.3 Morphology Analysis

Figure 5(a) shows the surface morphology of the control sample without ESP at 100 X magnification. In this morphology, a chain configuration is indicated as the PANI chain embedded within its matrix. An expanded coil of the PANI structure was also observed.[19] A major part of the PANI is compatible with 1-methyl-2-pyrrolidinone, which makes it soluble in the matrix, and hence, a flat surface was observed.

Figure 5(b) shows the surface morphology with a filler of 0.25 g of ESP at 100 X magnification. The distribution of the ESP particles in the polymer matrix is noticeably uniform. There are no large agglomerations of particles within the matrix. The chain of PANI is dissolved in the matrix and is compatible with ESP.[5] The average ESP particle size distribution obtained from the sieve instrument was 63 µm. The ESP particles are distributed far from each other because only a small amount of reinforcement was used.

Figure 5(c) shows the surface morphology with a filler of 0.75 g of ESP at 100 X magnification. The distribution of the ESP particles in the polymer matrix is noticeably uniform, but note that there are agglomerations of ESP on the surface of the sample. Agglomeration with PANI makes the connection of the conductive path more complete and improves conductivity.[6,20] A rougher surface was observed as filler loading was increased; the formation of microfiller was found due to difficulties of achieving a homogeneous dispersion of filler at high filler loading.[21]



(a) (b)

(c)

Figure 5: SEM micrographs of (a) without ESP; (b) 0.25g of ESP; (c) 0.75g of ESP.

3.4 X-ray Diffraction

XRD was used to determine the index of the diffraction pattern of the PANI-eggshell composites by assigning the correct Miller indices (hkl) to each peak (reflection) in the diffraction pattern, as shown in Figure 6. An XRD pattern is properly indexed when all of the peaks in the diffraction pattern are labelled and no peaks expected for the particular structure are missing.[22] All major peaks were accounted and assigned the correct Bravais lattice to calculate the lattice parameters for the PANI-eggshell composite. In cubic systems, the first XRD peak in the XRD pattern is due to diffraction from planes with the lowest Miller indices [i.e., simple cubic, (100), $h^2 + k^2 + l^2 = 1$; body centred cubic, (110), $h^2 + k^2 + l^2 = 2$; and face centred cubic (FCC), (111), $h^2 + k^2 + l^2 = 3$]. Because h, k and l are always integers, we can obtain $h^2 + k^2 + l^2$ values by dividing the 2sinθ values for the different XRD peaks with the minimum peak in the pattern (i.e., the 2sinθ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This calculation should yield a list of integers that represent the various values.[1] The correct Bravais lattice can then be identified by recognising the sequence of allowed reflections for cubic lattices (i.e., the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Figure 6 shows the X-ray diffraction pattern of amorphous materials in partially crystalline mixtures of conductive polymer. From the curve obtained and the calculation of interplanar spacing, Bravais lattice was found to be followed by a FCC pattern as shown in Tables 3 and 4. Therefore, the conductive polymer based on PANI was concluded to possess a FCC structure. The powders exhibited peaks at 2 angles, around 200 and 450, which indicates that the conductive polymer contains some crystalline domains.[10] The morphological structures of PANI derivatives are similar, closed-packed structures, which results in similar conductivity values.[23]

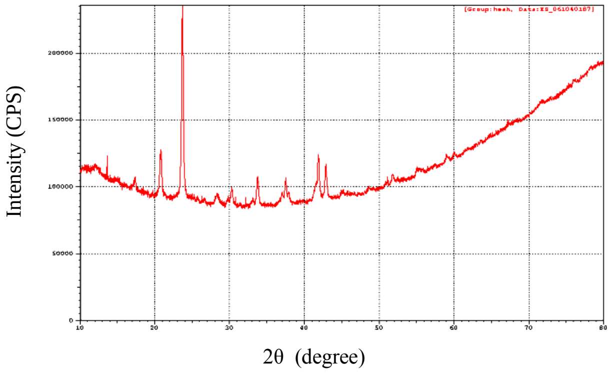


Figure 6: Graph shows the XRD diffractogram based on PANI-eggshell powder conductive polymer.

Table 3: Sequential of Bravais lattice for cubic system.

Primitive	1,2,3,4,5,6,8,9,10,11,12,13,14,16…
Body-centered	2,4,6,8,10,12,14,16…
Face-centered	3,4,8,11,12,16,19,20,24,27,32…
Diamond cubic	3,8,11,16,19,24,27,32…

Table 4: Calculation of interplanar spacing from the results interpreted from XRD.

Peak	2θ	θ	$\sin^2\theta$	$\sin^2\theta$ / $\sin^2\theta_{min}$	3 x $\sin^2\theta$ / $\sin^2\theta_{min}$	$h^2 + k^2 + l^2$	*hkl*	*d*
A	21.0	10.50	0.03321	1.0000	3.0000	3	111	7.318
B	23.9	11.95	0.04287	1.2909	3.8726	4	200	7.438
C	28.4	14.20	0.06018	1.8121	5.4363	5	210	7.019
D	30.3	15.15	0.0683	2.0566	6.1698	6	211	7.217
E	33.9	16.95	0.08499	2.5592	7.6775	8	220	7.471
F	37.5	18.75	0.10332	3.1111	9.3333	9	300	7.187
G	41.8	20.90	0.12726	3.8320	11.4959	11	311	7.159
H	43.0	21.50	0.13432	4.0446	12.1337	12	222	7.278

Notes: λ = 1.54 Å
n = 1
h = 1/x, k = 1/y, 1 = 1/z (from the Miller index)
Bravais lattice is FCC
Average lattice parameter = 7.26071 Å

3.5 Electrical Conductivity

The polymer backbone in the PANI-ESP conducting polymers consists of a π-conjugated chain. The overlap of π-electrons is called conjugation because it leads to a sequence of alternating double and single bonds, resulting in unpaired electrons that are delocalised along the polymeric chain. PANI exhibits conductivity due to this conductive theory.[5]

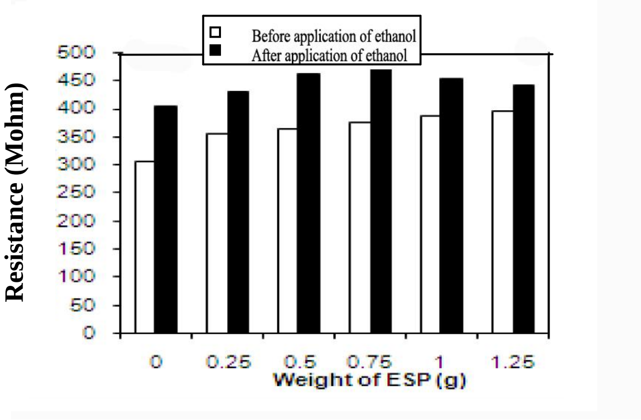
In this work, the conductive polymer was created for use as a sensor in several applications, such as in the detection of NH_3 gas, coffee aromas and ethanol. From the results shown in Figures 7(a), (b) and (c), the sensors were able to detect all three gases because there was either a significant increase or decrease in conductivity after application of those gases. This enabled the detection of these gases due to the differences in conductivity that were obtained. When the sensor was applied to ethanol, the highest resistivity change was obtained at 0.75 g of ESP, whereas the highest resistivity difference was obtained at 0.5 g ESP when coffee aroma was applied. This finding shows that the resistivity increased when these two gases were applied. However, when NH_3 gas was applied to the sensor, the resistivity value decreased significantly to about 25 M ohm, meaning that the conductivity increased significantly. Therefore, for comparison, the sensor is best used as an NH_3 gas detector because the conductivity was increased, which was the aim of this experiment. Resistivity, which is simply the inverse of the conductivity, was measured because the multimeter only shows resistivity values.[20]

Ethanol becomes ethylene (C_2H_4) gas, whereas ammonium hydroxide will become NH_3 when heated as it gives off a water molecule. When C_2H_4 gas, NH_3 gas and caffeine ($C_8H_{10}N_4O_2$) were brought into contact with the sensor, an interaction occurred between the structure of NH_3, C_2H_4 and caffeine that distorted the chemical structure of the PANI-ESP. Therefore, the conductive behaviour changes due to changes of the structure of the PANI-ESP. Due to structural distortion, the highest conductivity was shown upon application of NH_3 where it has the lowest resistivity [Figure 7(c)].

The conductivity of the conductive polymer was calculated according to the following formula using ASTM D257[20]:

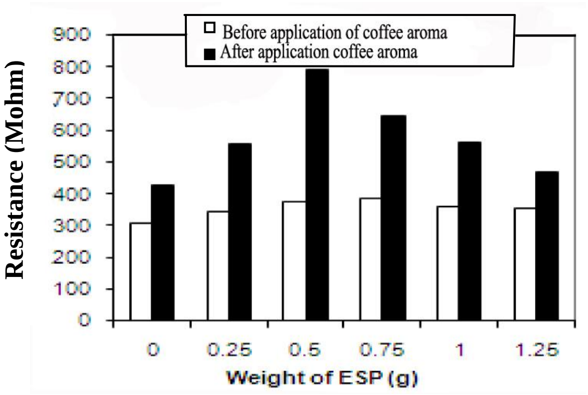
$$\text{Conductivity of a material,} \qquad \sigma = \frac{L}{R \times A} \qquad (3)$$

in which the conductivity is calculated from the resistance, R, between two sections separated by distance, L, having an average area, A. Table 5 shows the conductivity value calculated from this formula.

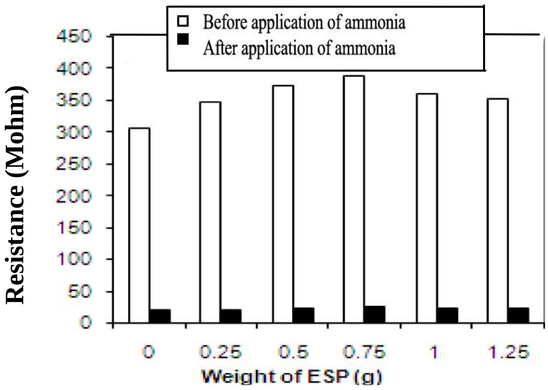


(a) Ethanol

Figure 7: Application of conductive test based on (a) ethanol; (b) coffee aroma; (c) ammonia gas (*continued on next page).*



(b) Aroma coffee



(c) Ammonia gas

Figure 7: *continued.*

Table 5: Conductivity calculated from the experimental.

Eggshell (g)	Conductivity, M (ohm^{-1} cm^{-1})					
	Ammonia		Coffee aroma		Ethanol	
	Before	After	Before	After	Before	After
0	7.44E-05	0.00113	7.44E-05	5.32E-05	7.44E-05	5.63E-05
0.25	6.59E-05	0.00106	6.59E-05	4.08E-05	6.42E-05	5.28E-05
0.5	6.12E-05	0.00093	6.12E-05	2.88E-05	6.25E-05	4.92E-05
0.75	5.89E-05	0.00089	5.89E-05	3.54E-05	6.09E-05	4.81E-05
1	6.32E-05	0.00097	6.32E-05	4.07E-05	6.38E-05	5.03E-05
1.25	6.46E-05	0.00103	6.46E-05	4.85E-05	6.63E-05	5.17E-05

4. CONCLUSION

The surface area and porosity of the ESP shows that reinforcement of filler into a PANI matrix enhances its conductive properties because it creates a different phase relative to the matrix materials that differs in its physical properties from the matrix of the conductive polymer. The distribution of the ESP particles in the polymer matrix was noticeably uniform, as shown by SEM micrograph. Agglomeration with PANI caused the connection of the conductive path to become more complete and improved conductivity behaviour. A rougher surface was observed as the filler loading was increased. On the other hand, the curve obtained by XRD showed that Bravais lattice was followed by a FCC pattern. Therefore, we concluded that the composite possessed a FCC structure. The conductivity test showed that the interaction that occurs between the structure of NH_3 gas, C_2H_4 gas and caffeine distorted the chemical structure of the PANI-ESP. Therefore, its conductive behaviour was altered due to structural changes. The highest conductivity was shown by application of NH_3, where it has the lowest resistivity. In summary, waste eggshells can be utilised as a potential improvement filler in conductive polymer composites.

5. REFERENCES

1. Callister, W. D. (2005). *Fundamentals of materials science and engineering*, 2nd ed. USA: John Wiley & Sons Inc.
2. Riande, E. & Diaz-Calleja, R. (2004). *Electrical properties of polymers*. New York: Marcel Dekker, Inc.
3. Askeland, D. R. & Phule, P. P. (2006). *The science and engineering of materials*, 5th ed. USA: Cengage Learning.
4. Min, G. (1999). Conducting polymers and their applications in the film industry – Polyaniline/polyamide blended films. *Synth. Met.*, 102(1–3), 1163–1166.
5. Bhadra, S., Khastgir, D., Singha, N. & Lee, J. H. (2009). Progress in preparation, processing and applications of polyaniline. *Prog. Polym. Sci.*, 34(8), 783–810.
6. Laska, J. & Pron, A. (1997). Conducting blends of polyaniline with conventional polymers. *Synth. Met.*, 84(1), 117–118.
7. Jacobo, S. E., Aphesteguy, J. C., Anton, R. L., Schegoleva, N. N. & Kurtyandskaya, G. V. (2007). Influence of the preparation procedure on the properties of polyaniline based magnetic composite. *Eur. Polym. J.*, 43(4), 1333–1346.
8. Jang, J. (2006). *Conducting polymer nanomaterials and their applications*. Seoul: Spinger-Verlag Berlin Heidelberg.

9. Gurunathan, K., Amalnerker, D. P. & Trivedi, D. C. (2003). Synthesis and characterization of conducting polymer composite (PAn/TiO_2) for cathode material in rechargeable battery. *Mater. Lett.*, 57(9), 1642–1648.
10. Gok, A., Omastora, M. & Prokes, J. (2007). Synthesis and characterization of red mud/polyaniline composites: Electrical properties and thermal stability. *Eur. Polym. J.*, 43(6), 2471–2480.
11. Suwanprateeb, J. (2000). Calcium carbonate filled polyethylene: Correlation of hardness and yield stress. *Composites Part A*, 31(4), 353–359.
12. Durcova, O., Michlik, P. & Knotek, L. (1989). Evaluation of the calcium carbonate dispersion in polypropylene composite fibres. *Polym. Test.*, 8(4), 269–275.
13. Tanniru, M. & Misra, R. D. K. (2005). On enhanced impact strength of calcium carbonate reinfored high-density polyethylene composites. *Mater. Sci. Eng. A,* 405(1–2), 178–193.
14. Nowaczyk, G., Glowin Kowski, S. & Jurga, S. (2004). Rheological and NMR studies of polyethylene/ calcium carbonate composites. *Solid State Nucl. Magn. Reson.*, 25(1), 194–199.
15. Wang, X., Tong, W., Li, W., Huang, H., Yang, J. & Li, G. (2006). Preparation and Properties of nanocomposite of poly (phenylene sulfide) / calcium carbonate. *Polym. Bull.*, 57(6), 953–962.
16. Maeda, S., & Armes, S. P. (1995). Surface area measurements on conducting polymer-inorganic oxide nanocomposites. *Synth. Met.*, 73(2), 151–155.
17. Fagerlund, G. (2006). Determination of specific surface by the BET method. *Mater. Struct.*, 6(3), 239–245.
18. Smith, B. C. (1999). *Infrared spectral interpretation: A systematic approach*, 1st ed. USA: CRC Press LLC.
19. Laska, J. (2004). Conformations of polyaniline in polymer blends. *J. Mol. Struct.*, 701(1–3), 13–18.
20. Kulshreshtha, A. K. (2002). *Handbook of polymer blends and composites*, 1st ed., vol. 2. UK: Rapra Technology Limited.
21. Supri, A. G. (2009). LDPE-isophthalic acid-modified eggshell powder composites, (LDPE/ESP). *J. Phy. Sci.*, 20(1), 87–98.
22. Smith, W. F. & IItashemi, J. (2006). *Foundation of materials science and engineering*, 4th ed. USA: McGraw Hill.
23. Gercek, B., Yaruz, M., Yilmaz, H., Sari, B. & Unal, H. I. (2007). Comparison of electrorheological properties of some polyaniline derivatives. *Colloids Surf., A,* 299, 124–132.