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Development and Investigation of Polyaniline Micro/nanocomposites that Possess Moderate Conductivity, Dielectric and Magnetic Properties

*By Sook-Wai PHANG and Noriyuki KURAMOTO**

As a nano-material possessing moderate conductivity, magnetic and dielectric property, novel hexanoic acid doped polyaniline (PAni/HA) micro/nanocomposites containing TiO_2 and Fe_3O_4 were prepared by template free method under various polymerization conditions. FT/IR spectra of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 indicated the peaks are derived from PAni/HA. The X-ray diffraction patterns of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 clearly showed the existence of both TiO_2 and Fe_3O_4. Nanorods/tubes shown in the SEM images indicated that PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites exhibited polymerization through elongation. The diameters of PAni/HA nanorods/tubes increased from 150–180 nm to 180–200 nm (PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4) after addition of Fe_3O_4 and TiO_2. PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 synthesized at 0 °C resulted large amount of nanorods/tubes compared with those synthesized at 25 °C. PAni/HA polymerized at low temperature exhibited higher conductivity (1.0×10^{-3} S/cm) compared with PAni/HA polymerized at higher temperature (7.0×10^{-4} S/cm). The conductivities of the PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 were relatively low ($3.3–4.2 \times 10^{-4}$ S/cm) after addition of TiO_2 and Fe_3O_4. PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites synthesized at 0 °C exhibited higher magnetization (Ms = 7.7 emu/g) compare with micro/nanocomposites that synthesized at 25 °C (Ms = 4.7 emu/g). TGA characterizations of the micro/nanocomposites were also being discussed in this paper.

KEY WORDS: Polyaniline / Micro/nanocomposites / Conductivity / Magnetization / Dielectric Constant /

Recently, micro/nanotubes or micro/nanowires have attracted considerable attention because of their unique properties and promising potential applications in nanodevices.[1–4] Conducting polymer as molecular wires (mico/nanowires) is an excellent choice because of their long π-conjugation length as well as their high metal conductivity (10^3–10^5 S/cm).[5] Among conducting polymers, polyaniline (PAni) and its analogues as micro/nanowires have been studied most extensively because their good environmental stability in both doped and undoped forms, low cost and ease of preparation, excellent physical and chemical properties, unique doping mechanism and its ease of protonic acid doping in the emeraldine form.[6,7]

A series of up to date methods have been reported for synthesizing micro-/nanotubes of conducting polymers, such as template synthesis, electrospining, chiral nematic reaction and molecular beam deposition.[8,9] However, template free method is an excellent route to synthesize the micro/nanotubes of conducting polymers because the micelle consists of dopant or dopant/aniline salt could act as a "soft template" in the formation of the nanostructured PAni by omitting the using of "hard template" (*e.g.* Al_2O_3 or polycarbonate). This method is easy and cheap due to the controllable diameter and length of the micro/nanotubes by alternating the synthesis parameters such as the types of dopants, polymerization temperature used and etc.[10–12]

Electromagnetic radiation is one of the byproduct of rapid development in space technology, navigation, telecommunications, aircraft technology and rapid proliferation of electronic devices. These rapid development and proliferation have generated pollution in the form of electromagnetic interference (EMI).[13] Generally, the active components commonly used in the traditional microwave absorbing and shielding material are dielectric and magnetic materials. Extensive study has been carried out to develop microwave-absorption materials and shielding materials with high efficiency. High conductivity, magnetic permeability and dielectric permmitivity of the materials contribute to high EMI shielding efficiency (SE) and good microwave absorbing property.[14] Thus, it is really a challenge to tailoring the synthesis parameters or additives used in order to synthesize a new series of PAni micro/nanowires possessing moderate conductivity, magnetic and dielectric properties.

The focus of this work is to develop and characterize a PAni micro/nanomaterial exhibits moderate conductivity, magnetic and dielectric properties. Recently, PAni/napthalene sulphonic acid/Fe_3O_4 nanocomposite was reported to exhibit good magnetic properties,[15] whereby PAni/HCl/TiO_2 nanocomposite was also reported to show a large dielectric constant.[16] Hence, PAni/Dopant/TiO_2/Fe_3O_4 nanocomposite should be an excellent microwave absorbing and shielding material because TiO_2 and Fe_3O_4 used in this study are the dielectric and magnetic filler that could enhance the dielectric and

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magnetic property of the PAni. Besides that, hexanoic acid used is the dopant which could improve the conductivity of the PAni. However, the preparation and characterization of such composite have not reported yet.

In this study, as a nano-material possessing moderate conductivity, magnetic property and dielectric property, novel hexanoic acid doped PAni (PAni/HA) micro/nanocomposites containing TiO_2 and Fe_3O_4 (PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4) were prepared by template free method using ammonium persulfate, APS as an oxidizing agent under various polymerization conditions. At the starting point of this research, weak acid such as hexanoic acid (HA) was chosen as a dopant because the acidity of the dopant will strongly effect the magnetization of the composites. Besides that, Fe_3O_4 microparticles was used instead of Fe_3O_4 nanoparticles because the spin magnet of Fe_3O_4 nanoparticles could not well align but just keep vibrating. These phenomena finally reduce the magnetization of Fe_3O_4 nanoparticles (Ms = 65 emu/g)[8] compared with Fe_3O_4 microparticles (Ms = 87 emu/g) that used in this study. PAni micro/nanocomposites were then characterized by FT/IR, X-ray diffraction (XRD) and thermogravimetric (TGA) analysis. Morphology studies of the micro/nanocomposites were investigated *via* SEM. Besides that, conductivity, magnetic and dielectric behaviors of the micro/nanocomposites were being studied in this communication.

EXPERIMENTAL

Aniline (Ani), n-hexanoic acid (HA) and ammonium peroxydisulfate (APS) used in this study were purchased from Kanto Chemicals. Tri-iron tetra-oxide microparticles (Fe_3O_4) with particle size of 1 μm (purity 99%) and TiO_2 nanoparticles with particle size of 30 nm were ordered from Soekawa Chemicals and Tayca Corporation respectively. The crystal phase of TiO_2 used this study is in anatase form because it is economical and anatase form of TiO_2 easily dispersed in water based systems or aqueous systems. Water used for polymerization was purified by distillation. Other reagents were used as received without purification unless noted.

In this study, hexanoic acid doped polyaniline (PAni/HA) micro/nanocomposites containing TiO_2 and Fe_3O_4 (PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4) were prepared by template free method using APS as an oxidizing agent under various polymerization conditions.

First, HA (1.0×10^{-2} mol) and Ani (1.0×10^{-2} mol) were mixed vigorously in distilled water for 30 min. Then, 0.10 g of TiO_2 (nanoparticles, 30 nm) and 0.10 g of Fe_3O_4 (microparticles, 1 μm) were added into the solution under sonication in order to obtain an emulsion of Ani/HA complex containing TiO_2 and Fe_3O_4. The emulsion of Ani/HA complex containing TiO_2 and Fe_3O_4 was mixed vigorously under ultrasonic action for 4 h to disperse TiO_2 and Fe_3O_4 well into the Ani/HA mixture before polymerization. APS aqueous solution was added dropwise in the mixture at 0 °C within 2 h. The Ani/HA/APS ratio used is 1/1/1. After addition of APS, the mixture was stirred under sonication for 1 h. Polymerization was continued (undisturbed) for 12 h by maintaining the temperature at 0 °C in the ice bath. The micro/nanocomposites were washed with distilled water and methanol three times, respectively. The nanocomposites were then dried in vacuum for 24 h.

The same polymerization method was repeated for PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite (with and without TiO_2 and Fe_3O_4) at room temperature (considered as 25 °C).

The characterizations of the PAni micro/nanocomposites were carried out by FT/IR, XRD, thermogravimetric analysis (TGA) and SEM. The FT/IR measurements in KBr in discus shape were taken by Shimadzu FT/IR (type 8100 M) spectrometer in between 400–4000 cm^{-1}. The X-ray diffraction patterns of the PAni micro/nanocomposite were recorded using RINT2000 Wilder-angle goniometer using Cu Kα radiation. Thermograms of the PAnis were recorded using Mettler-Toledo 851 thermogravimetric analyzer, in the presence of N_2 atmosphere from room temperature to 600 °C with heating rate of 10 °C/min. Particles sizes and morphology behaviors of the PAni micro/nanocomposite were determined from scanning electron microscope, SEM (JSM-6300F).

Samples used for conductivity measurements were in discus shape form with diameter of 10 mm and thickness of 0.3–0.5 mm. The sample was compressed slowly using a constant load of 100 kg and the whole process took around 5–10 min. Samples obtained with compacted density of 1.09×10^3 kg/m^3 were tested using a standard four-probe method (model Loresta HP).

The relative dielectric constants (ε_r) are obtained from the measurements of capacitance (C) and dissipation factor (D) by a 4192A LF Yokogawa Howlett Packard impedance analyzer in the frequency range of 5 Hz to 13 MHz. Samples used for the measurement were in discus shape that coated with the silver paste. The role of the silver paste is as the electrical contacts during measurement. The permittivity of the material is evaluated by the relation $C = \varepsilon s' A/t$, in which t is the thickness of the samples and A is the area of the discus shape's surface. The relative dielectric constant, ε_r is calculated from $\varepsilon_r = \varepsilon_s'/\varepsilon_o$.

Magnetization of PAni samples at magnetic field from -1.0×10^4 Oe to 1.0×10^4 Oe were measured at room temperature by vibrating sample magnetometer (VSM), model 1660 signal processor.

RESULTS AND DISCUSSION

The FT/IR spectra of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites are shown in Figure 1. The peaks at 1572 cm^{-1} and 1497 cm^{-1} are representing the quinoid and bezenoid ring, while the peaks at 1300 cm^{-1} and 1248 cm^{-1} are indicating the C-N stretching vibration of PAni. The peak at 1148 cm^{-1} is due to quinoid unit of doped-PAni. The stretching of CH_3 and CH_2 at 2928 cm^{-1} and 2853 cm^{-1} as well as the vibration mode of C=O at 1750 cm^{-1} are corresponding to the HA that used as the dopant

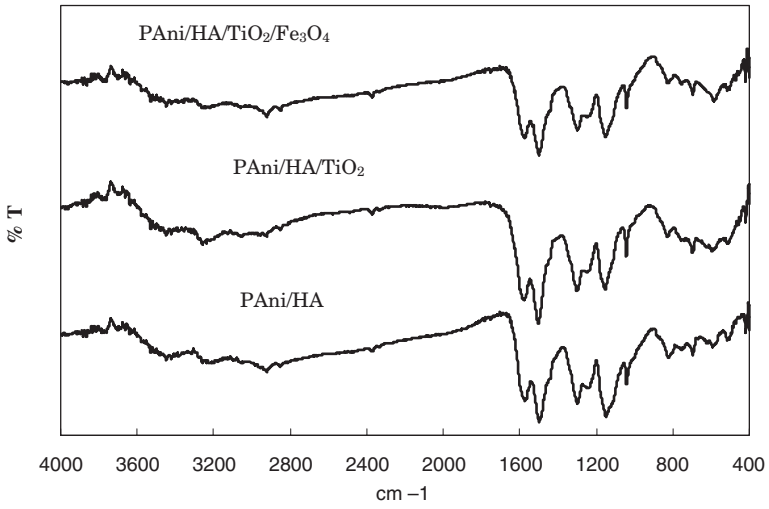

Figure 1. FT/IR spectra of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites.

in this study.[9] The peaks that mentioned above existed in all PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites that synthesized during this study. For PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite, the band at 598 cm^{-1} is attributed to the presence of the Fe_3O_4.[17] The incorporation of TiO_2 in the nanocomposites leads to small shift of FT/IR peaks in the nanocomposites.[16]

The X-ray diffraction patterns of the PAni micro/nanocomposite were recorded by Wilder-angle goniometer using Cu Kα radiation. Refer to the X-ray diffraction patterns shown in Figure 2, PAni/HA showed amorphous behavior with three major peaks for the characterization of doped-PAni. The peak at $2\theta = 7.0^\circ$ is ascribed to the periodicity distance between the HA dopant and N atom of PAni on adjacent main chains of PAni/HA. However, the peaks at $2\theta = 20.3^\circ$ and 25.0° are assigned as the periodicity parallel and perpendicular of the chain direction of the PAni chains.[9] On the other hand, both PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites indicated the presence of TiO_2 as predicted by the peaks belong to TiO_2 such as $2\theta = 25.3^\circ$ and 48.0°.[18,19] In the PAni micro/nanocomposite, the crystal phase of the TiO_2 is not changed because the characteristic peaks of TiO_2 are remained the same even after polymerization as shown by the X-ray diffraction patterns. Furthermore, the existence of Fe_3O_4 in PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites was also determined by the peaks belong to Fe_3O_4 such as $2\theta = 35.4^\circ$, 30.1°, 18.3°, 43.1° and 57.0°.[20,21]

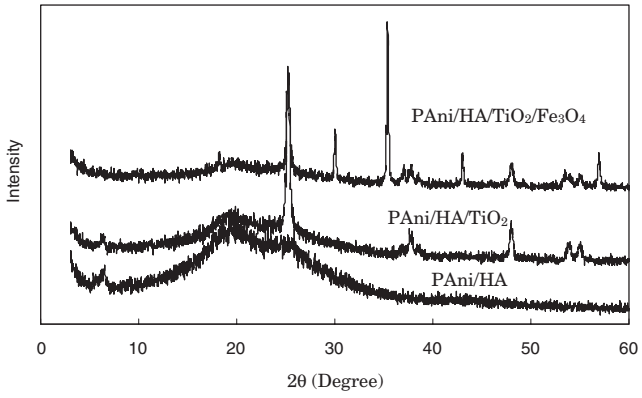

Figure 2. X-Ray diraction patterns of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites.

The thermal stability of PAni micro/nanocomposites were recorded by using thermogravimetric analysis. The thermogram obtained is shown in Figure 3 from room temperature to 600 °C. In TGA profile of PAni micro/nanocomposites, major losses of weight were observed over four temperature periods. Generally, the first decrease of weight loss from room temperature to 100 °C is attributed to the evaporization of water molecules or moistures and also the loss of possible impurities such as remaining monomer. The second stage observed from 100 °C to 230 °C is due to the loss of the HA dopant from PAni chains. The third stage from 230 °C to 350 °C is responsible for the dedoping of HA dopant from backbone of PAni. Finally, the last stage observed from 340 °C onwards is attributed to the complete degradation and structural decomposition of PAni. In the temperature range of 100 °C to 350 °C, the weight loss of PAni/HA/TiO_2 is greater than PAni/HA while PAni/HA/TiO_2/Fe_3O_4 is more thermally stable than PAni/HA and PAni/HA/TiO_2. It can be explained by the fact that a strong interaction exists at interface of TiO_2 and PAni weakens the interactive force of PAni interchains and finally fasten the thermal decomposition of PAni in the composites.[22] However, existence of Fe_3O_4 in the mico/nanocomposites significantly enhanced the interactive force of PAni chain and also the interaction between PAni with TiO_2, thus improved the thermal stability of the PAni/HA/TiO_2/Fe_3O_4 mico/nanocomposites if compared with mico/nanocomposites without addition of Fe_3O_4. The contents of Fe_3O_4 in PAni/HA/TiO_2/Fe_3O_4 mico/nanocomposites synthesized at 0 °C are higher (25%) compared with synthesized at 25 °C (10%) as indicated by the TGA profile below. Although the mass of Fe_3O_4 adding into the PAni/HA/TiO_2/Fe_3O_4 mico/

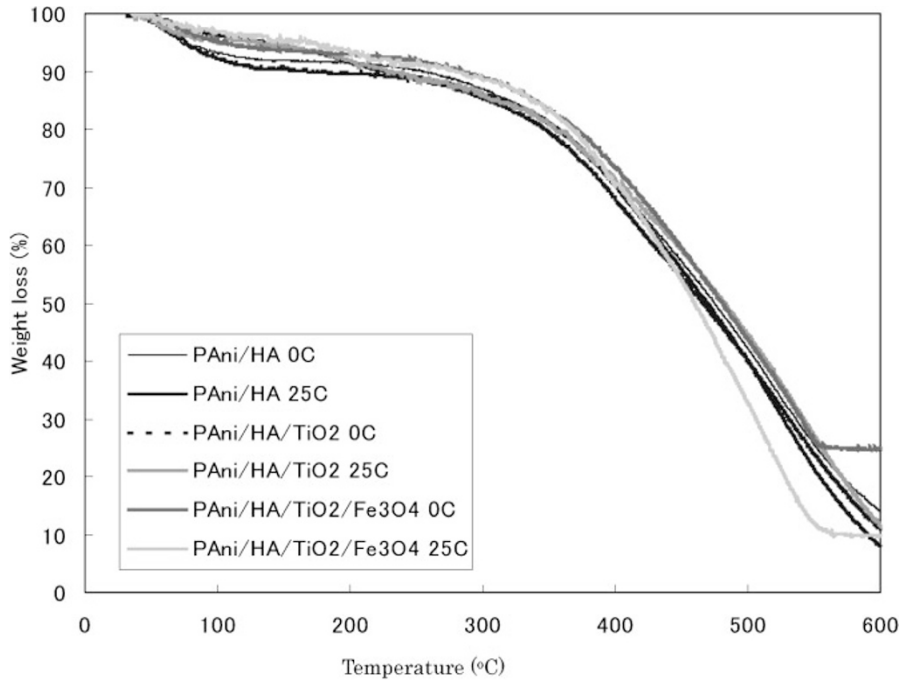

Figure 3. Thermograms of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites.

nanocomposites synthesized at 0 °C and 25 °C is same (0.1 g), Fe_3O_4 could easily interact with PAni to form the PAni/HA/TiO_2/Fe_3O_4 mico/nanocomposites at low temperature (0 °C) compared with high temperature (25 °C). This fact also can be proved by the magnetization data.

SEM images shown in Figure 4 indicated that Fe_3O_4 and TiO_2 micro/nanoparticles used in this study are ball-like shapes with diameter of 1 μm and 30 nm, respectively. During template free method, micelle composed of Ani/HA or Ani/HA/TiO_2 salt act as a "soft template" in order to form of the PAni nanotubes/rods (Figure 5). TiO_2 nanoparticles is believed to be existed in the center of the Ani/HA micelle to form the nanorods/tubes. On the other hand, Ani is assigned as the shell due to the hydrophobility of Ani and HA is acted as the tail of the micelles due to the hydrophilicity of –COOH of HA dopant. Since there is repulsive interactions of the "tail" group (HA group) of the micelle, thus the micelles are exist as a fluid surface and the spherical micelles are expected to form through aggregation process first before the formation of nanorods/tubes (through elongation) or spheres (through accretion) due to the lowest surface energy. Polymerization of these nanocomposites might take place in the micelle/water interface because APS oxidant used is water soluble. The micells become big sphere by accretion or tubes/rods by elongation depend on the synthesis conditions during polymerization process. For example, during template free method, polymerization of Ani/dopant under stirring process might form the PAni spheres, however, polymerization of Ani/dopant under undisturbed state might form the nanorods/tubes.[9]

Nanorods/tubes that shown in the morphology below indicated that PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites exhibited polymerization

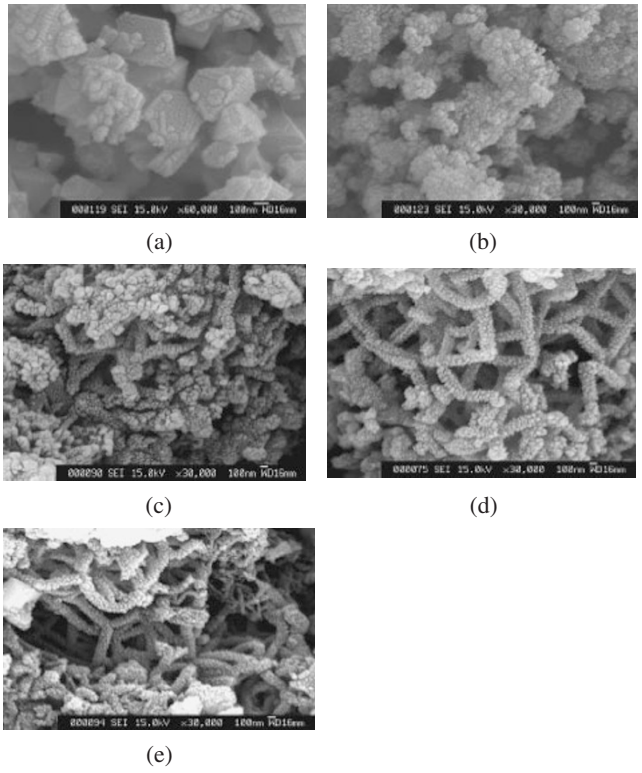

Figure 4. SEM images of (a) Fe_3O_4 microparticles (60,000x magnification), (b) TiO_2 nanoparticles (30,000x magnification) (c) PAni/HA, 0 °C (30,000x magnification) (d) PAni/HA/TiO_2, 0 °C mico/nanocomposites (30,000x magnification) and (e) PAni/HA/TiO_2/Fe_3O_4, 0 °C micro/nanocomposite (30,000x magnification).

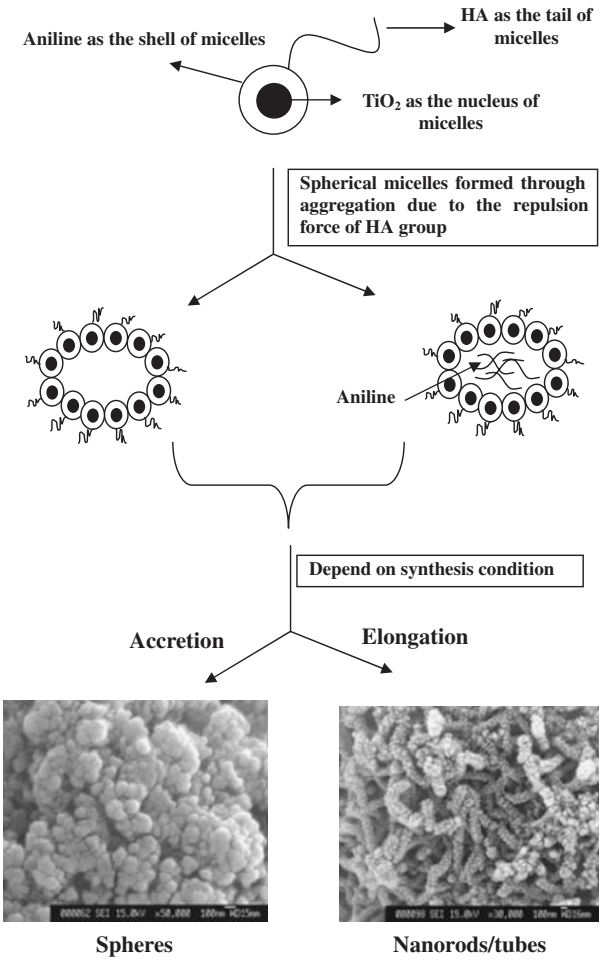

Figure 5. Schematic images for the formation of PAni spheres or PAni nanorods/tubes from the Ani/HA/TiO_2 micelle.

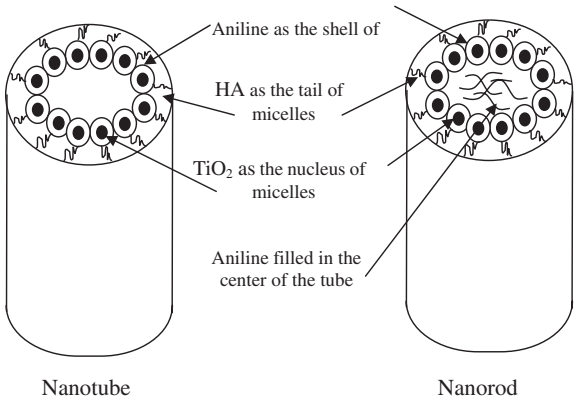

Figure 6. Schematic images for the resulted PAni/HA/TiO_2 nanorods/tubes through template free synthesis.

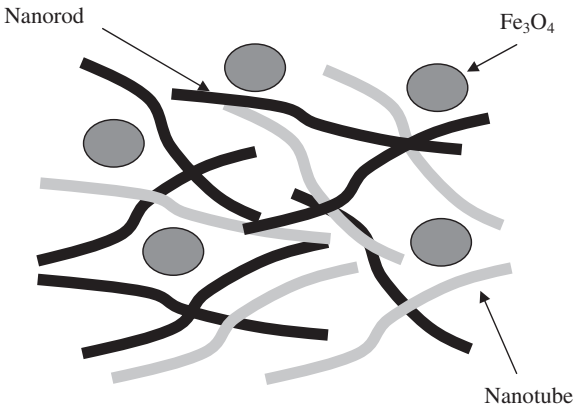

Figure 7. Schematic image of Fe_3O_4 physically mixed with PAni/HA/TiO_2 nanorods/tubes during template free synthesis.

through elongation. As shown in Figure 6, the micelle filled with aniline will form the nanorods while the micelle without aniline will form the nanotubes. The nanorods/tubes obtained in this study are formed by the Ani/HA micelles with TiO_2 as nucleus and Ani/HA micelles without TiO_2 as nucleus. So, the formations of the nanorods/tubes are not just depend on the TiO_2 content in the nanocomposites. The Ani/HA/TiO_2 micelle mechanism that proposed here agreed with the Ani/salicyclic acid/TiO_2 micelle mechanism that reported by Zhang *et al.*[11]

Fe_3O_4 microparticles are physically mixed with the PAni/HA/TiO_2 nanotubes/rods to form the PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites (Figure 7). The diameter of PAni/HA nanorods/tubes increased from 150–180 nm to 180–200 nm (PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4) after addition of Fe_3O_4 and TiO_2. PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 nanocomposites synthesized at 0 °C resulted large amount of nanorods/tubes compared with synthesized at 25 °C. It is because polymerization of nanocomposites at low temperature proceeded slowly and could form the nanorods/tubes easily compared with nanocomposites synthesized at higher temperature.

Refer to the SEM images in Figure 6, PAni/HA/TiO_2 resulted large amount of nanorods/tubes after addition of TiO_2 but the amount of nanorods/tubes significantly reduced after addition of Fe_3O_4. It is because addition of TiO_2 in the center of the Ani/HA micelle during template free method could activate the formation of nanorods.tubes. However, addition of Fe_3O_4 act as the barrier that disturbed the formation of the PAni nanorods/tubes from the Ani/HA micelles and thus reduced the amount of nanorod/tubes. In this situation, some of the micelles become big sphere (such as globular or ellipsoidal shapes) by accretion instead of elongation. Based on the results that discussed above, it is reasonable to convince that the morphology (amount of nanorods/tubes) and sizes of nanostructures (diameter of nanorods/tubes) are essentially affected by the synthesis parameter such as polymerization temperature and types of filler used. This result also agreed with the results that reported by Zhang *et al.* and Wan *et al.* in which the formation of the nanostructures are significantly depend on the synthesis condition such as reaction temperature, types of filler or dopant, concentration of dopant used and so on.[9,23]

Electrical conductivities of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites were recorded

Table I. Conductivities, relative dielectric constant (ε_r) and magnetization (Saturated magnetization (Ms), remnant magnetization (Mr) and coercive force (Hc)) of PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized at 0 °C and 25 °C

Sample Name	Conductivity (S/cm)	ε_r	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
PAni/HA (0 °C)	1.0×10^{-3}	—	—	—	—
PAni/HA (25 °C)	7.0×10^{-4}	—	—	—	—
PAni/HA/TiO_2 (0 °C)	4.2×10^{-4}	−5952	—	—	—
PAni/HA/TiO_2 (25 °C)	8.0×10^{-4}	2633	—	—	—
PAni/HA/TiO_2/Fe_3O_4 (0 °C)	3.3×10^{-4}	−7381	7.7	9.2×10^{-1}	122.7
PAni/HA/TiO_2/Fe_3O_4 (25 °C)	4.9×10^{-4}	1234	4.7	5.4×10^{-1}	121.6
Fe_3O_4	—	—	87.4	13.0	124.7

using four-probe method and the data were shown in Table I. Base on the data obtained, PAni/HA polymerized at low temperature exhibited higher conductivity (1.0×10^{-3} S/cm) compared with PAni/HA polymerized at higher temperature (7.0×10^{-4} S/cm). The conductivities of the PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites were relatively low ($3.3–4.2 \times 10^{-4}$ S/cm) after addition of TiO_2 and Fe_3O_4. During this study, TiO_2 and Fe_3O_4 that encapsulated in the PAni/HA matrix will partially block the PAni conductive path along the backbone of the PAni and lead to the decreasing in conductivity.

The relative dielectric constant (ε_r) (at 2.5 MHz) of PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized at 0 °C and 25 °C were recorded in Table I below. As a result, ε_r of PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized 25 °C is 2633 and 1234 respectively. Generally, the dielectric constants of polymers are very low and the addition of high dielectric constant material could significantly enhance the dielectric constant of polymeric systems. Recently, it had been found that large dielectric constant could be achieved near the percolation threshold of the composite.[24] The micro/nanocomposites that synthesized in this study consists of three materials that possessing different conductivities and permittivities. Thus, the interface across PAni/HA with TiO_2 and Fe_3O_4 may be sources that leading the large dielectric constant that posses by PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized 25 °C.[16] As reported by Chandrasekhar & Naishadham (1999), the high values of the dielectric constant are characteristics of conducting polymers which are partially attributed by the disordered motion of the charge carriers along the backbone of the conjugated polymer.[25]

On the other hand, ε_r of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized 0 °C is −5952 and −7381 respectively. The unique properties of so-called "left-handed" materials (LHM) with simultaneously negative real parts of the dielectric permmitivity ($\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r''$) and magnetic permeability ($\mu_r^* = \mu_r' - j\,\mu_r''$), (including the possibility of focusing the radiation of point sources by a plane-parallel plate) were predicted by Prof. V.G. Veselago in late 1960.[26] After that, various options were suggested for the practical realization of several types of composites with negative values of ε_r' and μ_r'. Although the negative dielectric constant is a new discovery in physic since year 2000 but the mechanism of this material is still not clear.[27–29] Negative value of dielectric constant will give rise to minimum transmission and maximum absorption that indicated good microwave absorbing property as reported by Smith *et al.* (2000).[30] Since the negative value of dielectric constant is a new discovery in physic since year 2000 and the mechanism of this material is still not clear, it is very difficult to explain why the negative dielectric constant is obtained at lower synthesis temperature instead of positive value.

Table I show the magnetization data on the applied magnetic field (from −10 kOe to 10 kOe) of Fe_3O_4 microparticles, PAni/HA/TiO_2/Fe_3O_4 nanocomposites synthesized at 0 °C and 25 °C. All the magnetization data recorded in Table I are saturated magnetization (Ms), remnant magnetization (Mr) and coercive force (Hc) that estimated from the magnetization curves. PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite (25 °C) under applied magnetic field at room temperature exhibited the hysteric loops (Figure 8) of the ferromagnetic behavior with the moderate saturation magnetization (Ms = 4.7 emu/g) and high coercivity (Hc = 121.6 Oe). Refer to all magnetization curves obtained, hysteresis loop appeared in Fe_3O_4 as well as PAni/HA/TiO_2/Fe_3O_4 nanocomposites synthesized at 0 °C and 25 °C that indicated PAni/HA/TiO_2/Fe_3O_4 nanocomposites show similar ferromagnetic behavior as Fe_3O_4 used in this study. For Fe_3O_4 microparticles, Ms, Mr and Hc are 87.4 emu/g, 13.0 emu/g and 124.7 Oe respectively. PAni/HA/TiO_2/Fe_3O_4 nanocomposites synthesized at 0 °C exhibited higher magnetization (Ms = 7.73 emu/g) compared with nanocomposites that synthesized at 25 °C (Ms = 4.67 emu/g). As conclusion, PAni/HA/TiO_2/Fe_3O_4 nanocomposites synthesized at 0 °C shows stronger magnetic behavior compared with synthesized at 25 °C. These phenomena can be explained by the fact that Fe_3O_4 could easily interact with PAni to form the PAni/HA/TiO_2/Fe_3O_4 mico/nanocomposites at low temperature (0 °C) compared with high temperature (25 °C) even the mass of Fe_3O_4 adding into both samples is same (0.1 g). This fact could be proved by the TGA profile discussed before.

CONCLUSIONS

In this communication, PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 were successfully synthesized through template free method under various polymerization conditions. FT/IR spectra of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 indicated the peaks are derived from HA doped PAni. The X-ray diffraction patterns of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites clearly showed the existence of both TiO_2 and Fe_3O_4. Thermal stability of the micro/nanocomposites was being studied by TGA analysis. Nanorods/tubes shown in the SEM images indicated that PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites exhibited polymerization through elongation. The diameters of PAni/HA nanorods/tubes increased from 150–180 nm to 180–200 nm (PAni/HA/TiO_2 and PAni/HA/TiO_2/

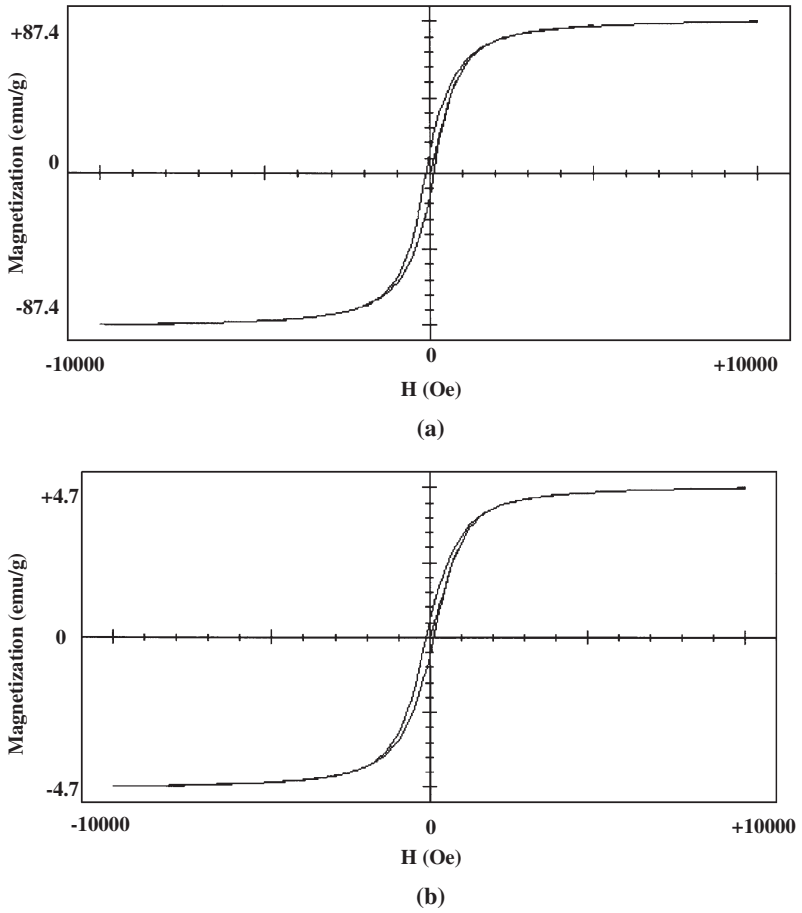

Figure 8. Variation of magnetization with the applied magnetic field measured at room temperature for (a) Fe_3O_4 and (b) PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized at 25 °C.

Fe_3O_4) after addition of Fe_3O_4 and TiO_2. PAni/HA, PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites synthesized at 0 °C resulted large amount of nanorods/tubes compared with those synthesized at 25 °C. PAni/HA polymerized at low temperature exhibited higher conductivity (1.0×10^{-3} S/cm) compared with PAni/HA polymerized at higher temperature (7.0×10^{-4} S/cm). The conductivities of the PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites were relatively low ($3.3–4.2 \times 10^{-4}$ S/cm) after addition of TiO_2 and Fe_3O_4 due to the blocking of conductive pathways by TiO_2 and Fe_3O_4 that embedded in the PAni matrix. Besides that, magnetic and dielectric behaviors of the micro/nanocomposites were measured by using vibrating sample magnetometer (VSM) and impedance analyzer respectively. As a result, ε_r of PAni/HA/TiO_2 & PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized 25 °C is 2633 and 1234 respectively. By contrast, ε_r of PAni/HA/TiO_2 and PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposite synthesized 25 °C is −5952 and −7381 respectively. PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites synthesized at 0 °C exhibited higher magnetization (Ms = 7.7 emu/g) compared with micro/nanocomposites that synthesized at 25 °C (Ms = 4.7 emu/g). As conclusion, PAni/HA/TiO_2/Fe_3O_4 micro/nanocomposites that posses moderate conductivity, high dielectric constant (or negative dielectric constant) and high magnetization that contribute to high EMI shielding efficiency (SE) and good microwave absorbing property have been successfully synthesized.

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