

**Multifunctional Polymer Nanocomposites with Core-Shell Structure for
Magnetoresistance and Electromagnetic Shielding**

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Doctor of Philosophy

Degree

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Abstract

The conductive polymer nanocomposites with different nanofillers were synthesized by a surface initiated polymerization (SIP) method. The electron transport mechanism of the conductive polymer nanocomposites was studied by the mott variable range hopping (VRH) model. All the synthesized samples showed 3-dimensional (3-D) VRH mechanism.

The nanofillers could affect the magnetoresistance (MR) behavior of polyaniline nanocomposites. Positive MR values of polyaniline nanocomposites with different carbon materials (graphene, carbon fiber, carbon tube and carbon black) were observed, the 2-D graphene/polyaniline nanocomposites showed higher MR than those of polyaniline nanocomposites with 1-D or 0-D carbon nanofillers. The MR of polyaniline nanocomposites with different magnetic nanoparticles was positive as well, and the CoFe_2O_4 (cobalt ferrite)/polyaniline nanocomposites showed higher MR than those of Fe@C /polyaniline and Fe_3O_4 (magnetite)/polyaniline nanocomposites at the same loading. However, negative MR was observed in the TiO_2 (titania)/polyaniline nanocomposites. The negative MR increased with increasing the TiO_2 loading in the polyaniline nanocomposites. The wave-function shrinkage model and forward interference model were applied to study the positive MR and negative MR of the polyaniline nanocomposites, respectively. The localization length, density of state at fermi level and average hopping length were affected by the nanofillers, loadings and magnetic field.

The enhanced electromagnetic shielding performance and thermal stability were observed in the Fe_3O_4 /polypyrrole nanocomposites. The highest shielding effectiveness

(SE) was -35.7 dB. The enhanced electromagnetic shielding performance was due to the dielectric loss, magnetic loss (eddy current loss) and improved impedance matching. Meanwhile, the improved thermal stability was induced by the covalent bonding formed between polypyrrole and epoxy matrix, enhanced char residue and nitrogen-containing material.

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Chapter 1. Introduction

1.1 Introduction

1.1.1 Composites

Composites are made from two or more materials with different properties and have the characteristics different from the individual components which remain separate and distinct within the finished structure. Composites are widely used in our daily life. For example, concrete is the most widely used composite in the world. In 2006, about 7.5 billion cubic meters of concrete were produced. And about 50 wt% of Boeing 787 Dreamliner is made of composites. Composites with any dimension in any phase less than 100 nm are called nanocomposites. Polymer nanocomposites consist of a polymer matrix having nanofillers dispersed in the polymer matrix.

1.1.2 Conductive polymer

In 1970s, Dr. Alan J. Heeger, Dr. Alan MacDiarmid and Dr. Hideki Shirakawa discovered the conductive polymer (polyacetylene), and the electrical conductivity of polyacetylene could be adjusted from insulator to metal.¹ Due to the evolutionary discovery, the Nobel Prize in chemistry in 2000 was awarded to them. Conductive polymer includes polyaniline, polypyrrole, polyacetylene, polythiophene, poly(DNTD) and poly(pphenylenebenzobisthiazole) (PBZT). Due to the low cost, light weight, high processability, mechanical flexibility, environmental stability, three distinct oxidation states (only for polyaniline), acid-base doping response and chemical functionalization capabilities,²⁻⁵ conductive polymers and their nanocomposites have been widely studied for different applications such as electromagnetic interference (EMI) shielding, energy storage, electrochromic devices, gas sensors and etc.⁶⁻¹⁰

1.1.3 Conductive polymer for magnetoresistance

Magnetoresistance (MR) is a phenomenon that reflects the resistance change of a material under an external magnetic field.^{11, 12} The MR is expressed as the following equation:

$$\text{MR \%} = \frac{R(H) - R(0)}{R(0)} \times 100$$

where $R(0)$ is the resistance without the magnetic field, and $R(H)$ is the resistance under the magnetic field H . The MR phenomenon can be found in different materials such as non-magnetic metal, magnetic metal, polymer and carbon materials.¹³⁻¹⁵ In 1856, the MR phenomenon was first discovered by Prof. William Thomson in iron and nickel.¹⁴ When the magnetic field is in the same direction as the current, the resistance of iron increases; when the magnetic field is perpendicular to the current, the resistance of iron decreases. In 1970s, the new technology was developed to synthesize very thin film of different materials, the thickness of the thin film was from nanometer to several micrometers. After that, in 1988, Dr. Albert Fert in France and Dr. Peter Grünberg in Germany independently discovered the GMR(80%) phenomenon in the multilayers films which contained alternating ferromagnetic and non-magnetic conductive layers.^{16, 17} In this thin film structure, the ferromagnetic Fe layer is separated by the non-magnetic Cr layer. The densities of state for up-spin and down-spin electrons are quite different, the scattering rate of the spin is proportional to the density of state. For the parallel-aligned magnetic layers, the up-spin electrons pass through the layers even without scattering, as the up-spin electrons are parallel to the magnetization of magnetic layers. However, the down-spin

electrons exhibit strong scattering, as the down-spin electrons are antiparallel to the magnetization. For the antiparallel-aligned multilayers, both up-spin and down-spin electrons are scattered in the magnetic layers, as the magnetization of the layers is different, so the spin must be antiparallel to the magnetization in one of the layers.¹¹ In 1997, the first read-out head for hard disk based on GMR phenomenon was developed. Until now, most of the read-out techniques are based on the GMR. Due to this great discovery, the Nobel Prize in physics in 2007 was awarded to Dr. Fert and Dr. Grünberg. In 2000, the extraordinary magnetoresistance (EMR) was discovered in the semiconductor-metal hybrid system, the EMR is about 1,000,000% at room temperature which is larger than other types of MR. There are some other types of MR reported in the literature such as anisotropic magnetoresistance (AMR), tunnel magnetoresistance (TMR), and colossal magnetoresistance (CMR).¹⁸⁻²⁰ The MR phenomenon can be applied for different applications such as novel programmable logic devices, hard disc drives, magnetoresistive random access memories (MRAM) and magnetic sensors.^{21, 22}

Due to the unique advantages of conductive polymers and development of MR effect, researchers have paid much attentions to the MR behavior of conductive polymers.²³⁻²⁵ In recent year, the MR behavior of polyaniline at different temperature was studied. In 1993, Heeger *et al.* discovered -100% MR in polyaniline film at 1.2K;²⁶ in 1998, Ghosh *et al.* reported the 30% MR in HCl doped polyaniline nanoparticles at 1.9K;²⁷ in 2004, Long *et al.* synthesized the polyaniline hollow microspheres, and the -12% MR was observed at 90 K;²⁸ in 2006, Long *et al.* reported the 91% MR in polyaniline nanotubes at 3K;²⁹ in 2010, Epstein *et al.* reported the 55% MR in polyaniline nanofibers at 2.5K;³⁰ in

2013, Nath *et al.* reported the polyaniline nanofibers with -1% MR at 300K.³⁰ However, the MR signal at room temperature of polyaniline is very low and there is few theoretical analysis for the MR behavior of polyaniline. Meanwhile, researchers also studied the MR behavior of polyaniline nanocomposites with different nanoparticles. Romero *et al.* reported the MR behavior of the magnetic polyaniline nanocomposites at different temperatures, the largest MR signal was only about 1.5%.³¹ Prabhakaran *et al.* reported the negative MR behavior in the polyaniline/bismuth ferrite nanocomposites.³² Bin *et al.* reported the negative MR (-7.5%) in the polyaniline coated carbon fabrics nanocomposites.³³ The MR behavior of polyaniline nanocomposites could be affected by nanofillers. However, there is less work about the nanofiller's type effect on the MR and how the nanofillers affect the MR of polyaniline nanocomposites. In this dissertation, the effects of nanofillers on the MR behavior of polyaniline nanocomposites were systematically studied, and the wave-function shrinkage model and forward interference model were applied to study the positive MR and negative MR, respectively. This study would provide the information on MR behavior of polyaniline and its nanocomposites with different nanofillers, the electron transportation mechanism in the polyaniline under the magnetic field, and how the nanofillers affect the electron transportation in the polyaniline matrix. More importantly, the effects of magnetic field and nanofillers on the localization length, density of state at fermi level and average hopping length were systematically studied, which would explain the MR behavior of polyaniline and its nanocomposites.

1.1.4 Conductive polymer for electromagnetic shielding

Due to the development of information technology, the electromagnetic waves at different frequencies have been widely used for different applications. For example, the electromagnetic waves have been deployed in wireless cell phones, local area networks and other communication facilities.³⁴ The demand for electromagnetic wave absorbers and electromagnetic wave absorbing materials is ever growing in military and civilian applications.^{35, 36} Modern electronics often generate severe electromagnetic radiation waves causing interference.³⁷ Thus, effective protection from electromagnetic radiation is needed. The shielding of electromagnetic wave can be achieved by either absorption or reflection, which can protect people from electromagnetic radiation and transport the electromagnetic signals away from the desired electronics. Great efforts have been made to develop high-performance electromagnetic shielding materials in the past decades.

Shielding effectiveness (SE) is a measure of the material's ability to attenuate electromagnetic energy. A higher SE indicates a better attenuation of electromagnetic wave energy. The electromagnetic SE is expressed in decibels (dB). The electromagnetic SE of 10, 20 and 30 dB corresponds to 90%, 99% and 99.9% reduction of electromagnetic wave, respectively.³⁸ The shielding requirements depend on the application. For example, 15-20 dB is an adequate level of shielding for laptop and desktop computers, workstation requires 30-40 dB and the cell phones require SE of 70–90 dB.^{38, 39} Different materials have been applied for electromagnetic shielding. Al-Saleh *et al.* reported the polystyrene nanocomposites with 1.3 vol% copper nanowire with a SE of 27 dB.³⁸ Liang *et al.* reported the 15 wt% graphene/epoxy composites with a SE of 21 dB.³⁶ Yang *et al.* reported the

carbon nanotube–polystyrene foam composites with a SE of 18.56 dB.⁴⁰ He *et al.* used the Fe/carbon nanotube-polypropylene for electromagnetic shielding (the SE is about 32 dB).⁴¹ Zhu *et al.* reported the Fe@FeO-polyurethane nanocomposites with a SE of about 20 dB.⁴² The current materials for electromagnetic shielding are metal and carbon based materials. However, these materials have some drawbacks. The disadvantages of metal and carbon based materials are high density, poor corrosion resistance, processing difficulty, high loading, high cost and limited SE.^{39, 43} And some materials were prepared with the assistance of solvent, which would limit the application of the materials.⁴² Due to the unique advantages of conductive polymers, researchers have paid attention to study the conductive polymers and their nanocomposites for electromagnetic shielding application. Recently, polypyrrole, one of the widely studied conductive polymers, has been studied for electromagnetic shielding. For example, Kim *et al.* synthesized PPy–nylon 6 composite fabrics for electromagnetic shielding (the shielding efficiency was dependent on the electrical conductivity and layer array sequence).⁴⁴ Avlioni *et al.* studied the polypyrrole-coated polyester nonwoven textiles with better electromagnetic wave shielding performance.⁴⁵ Although polypyrrole has some advantages for electromagnetic shielding application, there are two shortcomings. First, as non-magnetic material, only the dielectric loss can affect the electromagnetic shielding performance. Second, the dielectric permittivity and magnetic permeability are out of balance for polypyrrole, resulting in a bad impedance matching. In order to overcome these defects, the magnetic nanoparticles are needed. Among all the magnetic materials, magnetite (Fe_3O_4) is widely used because of its magnetic property, low toxicity, high biocompatibility and high Snoek's limit.³⁴ In

recent years, the electromagnetic shielding performance of polypyrrole with magnetic nanoparticles was reported. For example, Wang *et al.* reported the cobalt/polypyrrole nanocomposites with tunable electromagnetic properties because of the coexistence of magnetic loss and dielectric loss to electromagnetic waves.⁴⁶ However, there is less work about the electromagnetic shielding performance of PPy with Fe₃O₄ nanocomposites.

It is well known that the electromagnetic energy is transformed to joule thermal energy by the electromagnetic shielding materials. The thermal stability of the electromagnetic shielding materials is very important, since the generated joule thermal energy can induce the degradation of the electromagnetic shielding materials. So the flame retardant property is a vital parameter for the electromagnetic shielding materials in the practical application. Polypyrrole has shown its great potential as the flame retardant materials. For example, Zhang *et al.* reported the polypyrrole epoxy nanocomposites with reduced flammability.⁴⁷ In this dissertation, the enhanced electromagnetic shielding performance and thermal stability were observed in the PPy with Fe₃O₄ nanocomposites. The enhanced electromagnetic shielding performance was due to the dielectric loss and magnetic loss; meanwhile, and the enhanced thermal stability was studied as well.

1.2 Overview

In Chapter 2-4, the polyaniline nanocomposites with different nanofillers had been successfully synthesized by the surface initiated polymerization (SIP) method. The chemical structure of polyaniline nanocomposites was characterized by the Fourier transform infrared spectroscopy (FT-IR), the crystallinity of the nanocomposites was studied by the X-ray diffraction (XRD), the morphology of the nanocomposites was

analyzed by the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) was used to observe the nanoparticle dispersion in the polyaniline matrix. The electron transport mechanism of the polyaniline nanocomposites was studied by mott variable range hopping (VRH) model. The MR behavior of the polyaniline nanocomposites was studied by the wave-function shrinkage model and forward interference model. Chapter 5 was the mechanical property and electrical property of polyaniline epoxy nanocomposites fabricated by different methods. And the loading effect of polyaniline on the mechanical property and electrical conductivity was reported as well. Chapter 6 studied the electromagnetic shielding performance and thermal stability of polymer nanocomposites with polypyrrole functionalized magnetite nanoparticles. The Conclusions are provided in Chapter 7.

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**Chapter 2. Tunable Magnetoresistance of Core-Shell Structured
Polyaniline Nanocomposites with 0, 1 and 2 Dimensional Nanocarbons**

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Abstract

Magnetoresistance (MR) behaviors of polyaniline (PANI) nanocomposites were adjusted with the assistance of the 0, 1 and 2 dimensional carbon nanofillers (carbon black, carbon fiber, carbon nanotube and graphene). The PANI nanocomposites were synthesized by a facial surface initiated polymerization method. The enhanced thermal stability were noticed in these carbon based PANI nanocomposites. Meanwhile, the enhanced dielectric constant was observed in the PANI nanocomposites compared to pure PANI, indicating these materials have potential for electromagnetic interference shielding and energy storage. A quasi 3-d electron conduction mechanism was observed in all PANI nanocomposites through the Mott variable range hopping (VRH) model. The responses of the localization length, density of state at fermi level, average hopping length and hopping energy of the PANI nanocomposites with different morphological carbon nanofillers to the magnetic field were studied by a wave-function shrinkage model.

2.1 Introduction

Magnetoresistance (MR) is the electrical resistance change of the materials in response to an external magnetic field. Generally, the MR is classified to giant magnetoresistance (GMR), anisotropic magnetoresistance (AMR), tunnel magnetoresistance (TMR) and etc. Based on the development of the thin film technology in 1970s, the GMR was discovered in the coupled multilayers of Fe/Cr in 1988.^{1, 2} In this thin film structure, the ferromagnetic Fe layer was separated by the nonmagnetic Cr layer. The densities of state for up-spin and down-spin electrons are quite different, the scattering rate of the spin is proportional to the density of state. For the parallel-aligned magnetic layers, the up-spin electrons could pass through the layers even without scattering, as the up-spin electrons are parallel to the magnetization of magnetic layers. However, the down-spin electrons exhibit strong scattering, as the down-spin electrons are antiparallel to the magnetization. For the antiparallel-aligned multilayers, both up-spin and down-spin electrons would be scattered in the magnetic layers, as the magnetization of the layers is different, so the spin must be antiparallel to the magnetization in one of the layers. The AMR signal depends on the direction of the magnetic field. For example, in the nickel-copper alloys, when the magnetic field is parallel to the electron current, which means the magnetic moment is parallel to the direction of electron current, the scattering of the electrons would be very strong, hence a higher resistivity is observed; when the magnetic field is oriented transverse to the electron current (then the magnetic moment is oriented transverse to the electron current), then the scattering of the electron is very weak, hence a lower resistivity is observed.³ TMR is observed in the magnetic tunnel junction (MTJ)

(two ferromagnets separated by a thin insulator) and is defined as $TMR = \frac{R_{ap}-R_p}{R_p}$ (R_{ap} , resistance in the antiparallel state; R_p , resistance in the parallel state).^{4, 5} The MTJ's resistance depends on the relative orientation of the magnetization of two ferromagnets (relatively lower resistance for parallel alignment and relatively higher resistance for antiparallel alignment).⁴ In addition, researchers also discovered that some 3d transition-metal oxides exhibit large MR since their unique property (metal to insulator transition), the MR in these materials is very large, which is named as colossal magnetoresistance (CMR). The mechanism of CMR is still open for discussion.⁶⁻⁹ The interest for the MR phenomenon stems from its great potential for different applications such as novel programmable logic devices, hard disc drives, magnetoresistive random access memories (MRAM), magnetic sensors and etc.^{1, 10-13} Therefore, the research work related to the MR phenomenon have significant effect on the industry and our daily life.

Due to low manufacturing cost, easy processability, unique mechanical flexibility, light weight (compared to metal), controllable electrical conductivity (insulator to metal) and chemical functionalization capabilities,¹⁴⁻¹⁷ intrinsically conductive polymers (polyaniline, polypyrrole, polythiophene, PEDOT and etc) have attracted much research attention in the past decades and can be applied for different applications such as energy storage (supercapacitor and solar cell), environmental remediation (electromagnetic interference (EMI) shielding and heavy metal (such as Cr(VI)) removal, antistatic or anticorrosive coating, electrochromic devices (reversible color switching window) and etc.¹⁸⁻²⁶ Among the conductive polymers, researchers paid much more attention to polyaniline (PANI), because it has unique chemical structure, widening its applications in

different areas. PANI has three different oxidation structure including leucoemeraldine, emeraldine and (per)nigraniline. Only the emeraldine based form doped with acids shows electrical conduction. Hence, researchers paid much work to the emeraldine based form. In recent years, new applications of PANI have been developed, for example, Gu *et al.* used H₃PO₄ doped PANI as a coupling agent to enhance the particle dispersion quality in the thermosetting materials, meanwhile, the enhanced flame retardant property was observed.²⁷

Since wide applications of the MR technology and unique advantages of PANI, the MR phenomenon in PANI and its nanocomposites has attracted more attention to further improve and develop the MR applications to meet the rigorous requirements in some fields. For example, the aerospace and auto manufacturing have hard standards for the weight of materials.¹⁴ In order to improve the MR behavior of PANI, different nanofillers were added into the PANI matrix. Until now, the MR behaviors of PANI and its nanocomposites with different nanofillers have been reported. For instance, Romero *et al.* reported the MR behavior of the magnetic PANI nanocomposites at different temperature, the largest MR signal was about 1.5%.²⁸ Prabhakaran *et al.* reported the negative MR behavior in the polyaniline/bismuth ferrite nanocomposites.²⁹ Gu *et al.* discovered the MR signal transformed from positive to negative in the silica/PANI nanocomposites, and reported the MR behavior of the carbon nanotube/PANI nanocomposites.^{30,31} The carbon nanomaterials with different morphology (0-D carbon black, 1-D carbon fiber, 1-D carbon nanotube and 2-D graphene) possess good thermal stability, electrical conductivity, mechanical property and chemical resistance.³² Li *et al.* studied the polypropylene nanocomposites with various

carbon nanostructures with enhanced thermal stability and higher crystallinity.³³ Zhu *et al.* reported the polypyrrole nanocomposites with different carbon nanostructures with negative permittivity.³⁴ However, there is less work about the nanofiller's morphology effect on the MR behavior of PANI nanocomposites.

In this work, the PANI nanocomposites with different morphological carbon nanomaterials were synthesized by the surface initiated polymerization (SIP) method. The Fourier transform infrared (FT-IR) spectroscopy was used to characterize the chemical structure of PANI and its nanocomposites. The thermal stability of the PANI nanocomposites was studied by thermogravimetric analysis (TGA). The morphology of the PANI nanocomposites was characterized by the scanning electron microscope (SEM). The effect of the carbon nanofillers on the crystallinity of PANI was studied by X-ray diffraction as well. The frequency-dependent permittivity at room temperature, temperature dependent resistivity of the PANI nanocomposites and MR were systematically investigated. The mott variable range hopping (VRH) model was applied to study the electrical conduction mechanism of the PANI nanocomposites. The positive MR signal of the PANI nanocomposites was controlled by the carbon nanofiller morphology and loadings at room temperature. The wave-function shrinkage model was applied to study the MR behavior of the PANI nanocomposites. Meanwhile, the magnetic field effects on the localization length, density of state at fermi level, average hopping length and average hopping energy were reported as well.

2.2 Experimental

2.2.1 Materials

Aniline (C_6H_7N), ammonium persulfate (APS, $(NH_4)_2S_2O_8$, 98%) and *p*-toluene sulfonic acid (PTSA, $C_7H_8O_3S$, $\geq 98.5\%$) were purchased from Fisher Scientific. The carbon blacks (average particle size: 42 nm) were provided by Stream Chemical, Inc. from MA, USA. The carbon fibers (average diameter: 150 nm, surface area: 20-30 m^2/gm) were provided by Pyrograf Products, Inc. from Ohio, USA. The multi-walled carbon nanotubes (OD: 5-12 nm, length: 30-50 μm) were purchased from Timenano, Inc. from China. The graphene (thickness: 10-20 nm, x-y dimensions of 14.0 μm) were obtained from Angstrom materials, Inc. OH, USA. All the chemicals were used as-received without any further treatment.

2.2.2 Fabrication of PANI nanocomposites with carbon nanomaterials

The PANI nanocomposites were fabricated using the SIP method. Firstly, the carbon nanomaterials (carbon black, fiber, tube or graphene) were dispersed in an aqueous solution containing PTSA (30 mmol) and APS (18 mmol) in 200 mL deionized water by 1 hour sonication and mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) in an ice-water bath. Secondly, the aniline solution (36 mmol, 50 mL deionized water) was mixed with the above carbon nanomaterials suspension and mechanically and ultrasonically stirred for additional 2 hours in the ice-water bath for polymerization. The product was vacuum filtered and washed with deionized water several times to remove any unreacted PTSA and APS, then washed with ammonia solution to dedope the PANI nanocomposites, then redoped with 1 M PTSA solution. The final

synthesized nanocomposites were dried at 50 °C in oven overnight. The graphene/PANI nanocomposites with a graphene loading of 5.0, 10.0, 20.0, and 40.0 wt% were fabricated, carbon fiber/PANI nanocomposites with a fiber loading of 5.0, and 10.0% were synthesized, and carbon nanotube/PANI nanocomposites with a carbon nanotube loading of 10.0 and 20.0 wt% were synthesized. Pure PANI was fabricated following the above procedures without adding any nanoparticles for comparison.

2.2.3 Characterizations

The morphology of the as-synthesized materials was examined by a FEI Helios NanoLab 600i scanning electron microscopy (SEM, Hillsboro, OR). All the samples were sputter coated with a thin layer of carbon (about 3 nm) to ensure good imaging. The FT-IR spectra of the products were obtained on a Nicolet IS 10 (in the range from 650 to 2000 cm^{-1} at a resolution of 4 cm^{-1}). The XRD was measured by D/max-rB wide-angle X-ray diffractometer at a $\text{Cu } k_{\alpha}$ wavelength of 0.154 nm. The scanning rate is 4 ° min^{-1} from 10 to 80°. TGA was performed using TA Instrument TGA 2950 under air-flow rate of 60 mL min^{-1} from 30 to 1000 °C with a heating rate of 20 °C/ min. Raman spectra were performed on a Princeton Instrument (Acton Trivista 555 spectrometer with laser excitation at 532 nm). Dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of 20 to 2×10^6 Hz at room temperature. The pure PANI and its nanocomposites with different carbon nanofillers were pressed in a form of disc pellet with a diameter of 25 mm by a hydraulic presser. The same samples were also used to measure the resistivity and MR. The temperature dependent resistivity was measured by a standard four-probe method from 50 to 290 K. **Figure 2.1**

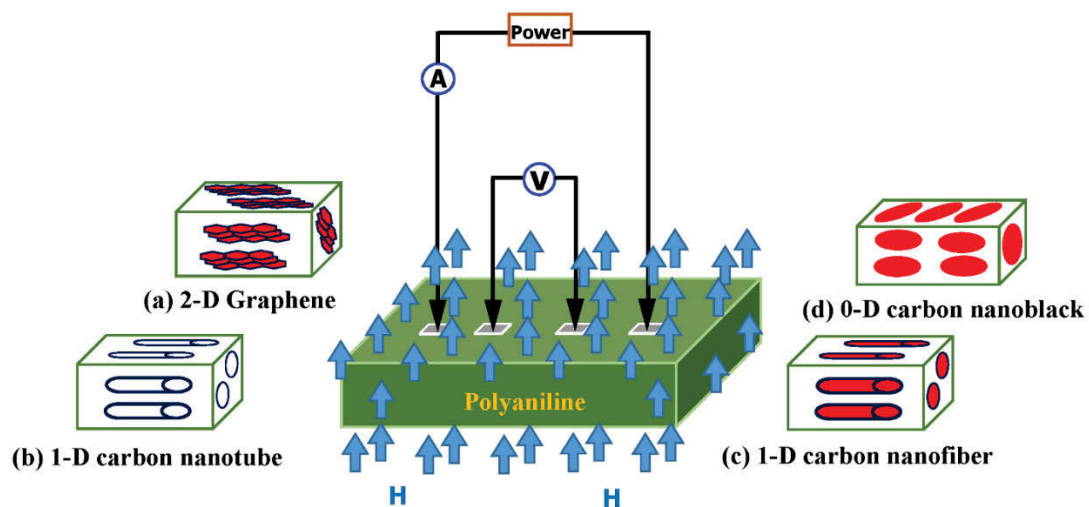


Figure 2.1 MR measurement for the pure PANI and its nanocomposites with different carbon nanofillers.

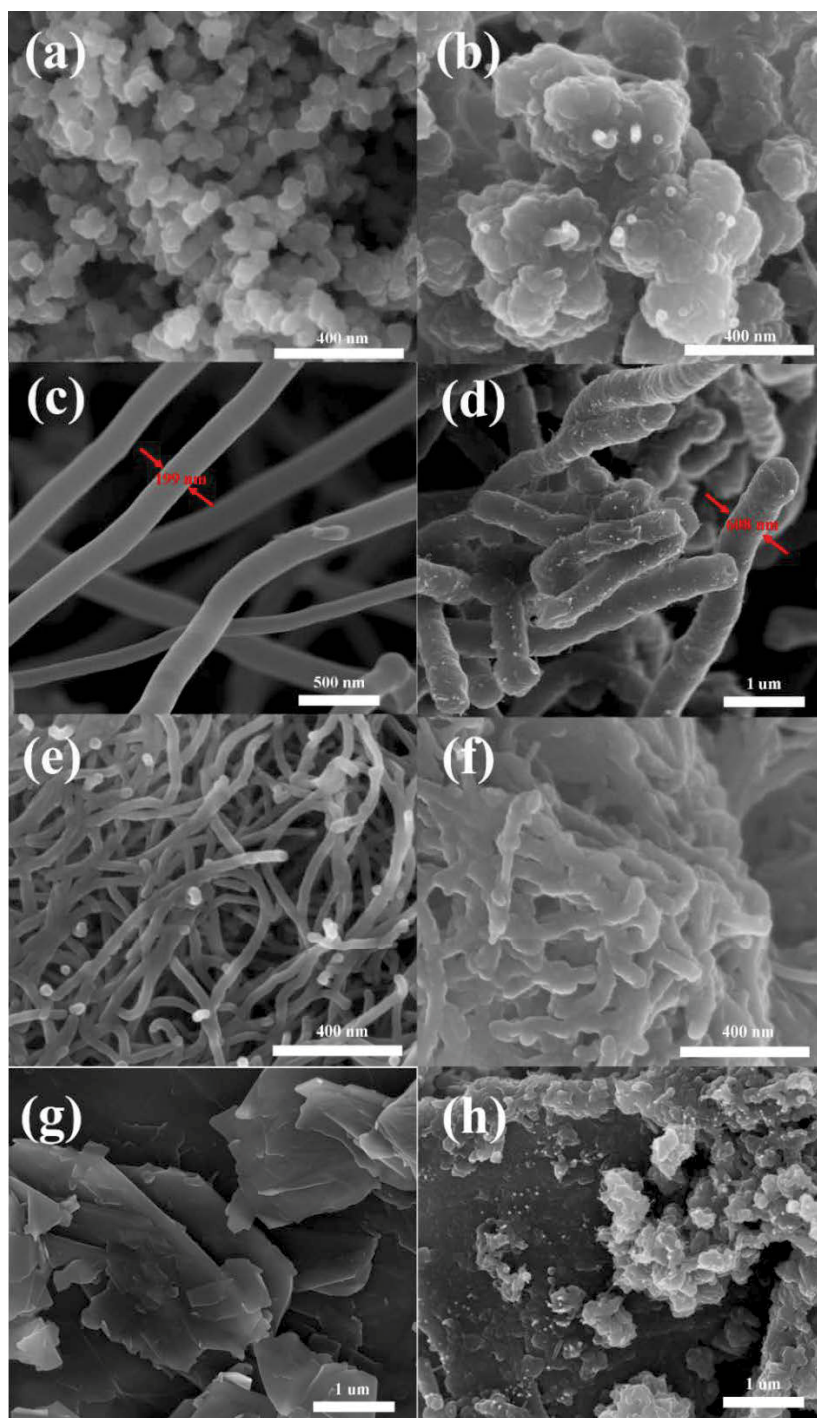


Figure 2.2 SEM images of (a) carbon black, (b) carbon black/PANI, (c) carbon fiber, (d) carbon fiber/PANI, (e) carbon nanotube, (f) carbon nanotube/PANI, (g) graphene, and (h) graphene/PANI nanocomposites.

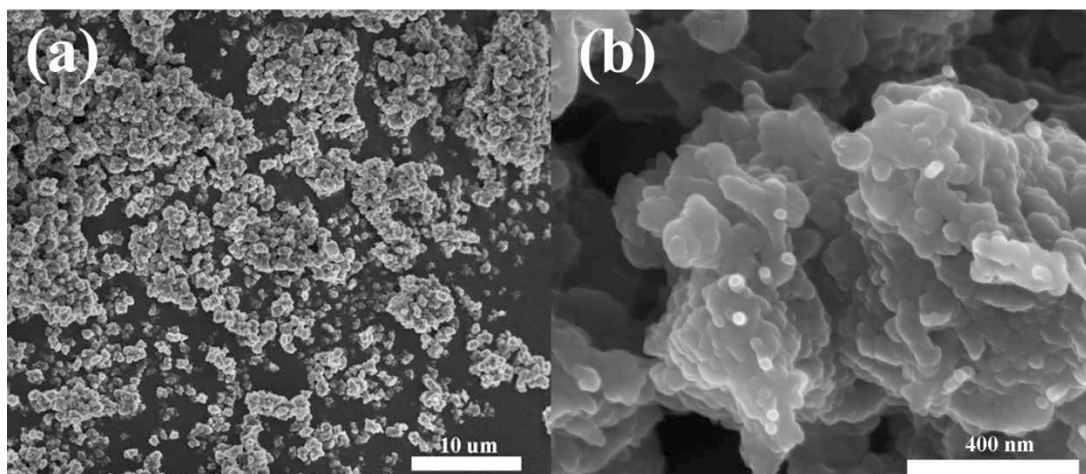


Figure 2.3 SEM images of pure PANI.

shows the MR measurement of the PANI nanocomposites which was carried out using a standard four-probe technique by a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design at 290 K.

2.3 Results and discussions

2.3.1 Microstructure characterization

The SEM images of pure PANI, pure carbon nanofillers, and PANI nanocomposites with different carbon nanofillers are shown in **Figure 2.2&2.3**. In **Figure. 2.3(a)**, the PANI particles are sphere-like and uniform. Under the higher resolution, the rough and flake-like surface of PANI is observed, **Figure 2.3(b)**.³⁵ The surface of the carbon black is very smooth with an average diameter about 56 nm measured by Image software, **Figure 2.2(a)**. After coated by PANI, the surface of carbon black, **Figure 2.2(b)**, becomes rougher and flake-like, indicating the PANI coating on the surface of the carbon black nanoparticles. The surface of carbon fiber, **Figure 2.2(c)** and carbon nanotube, **Figure 2.2(e)**, are relatively smooth. However, **Figure 2.2(d&f)** exhibit that the surface of carbon fiber/PANI and carbon nanotube/PANI nanocomposites become rough after the polymerization of the aniline monomer on the surface of the particles. The average diameter of carbon nanofiber/PANI is about 608 nm measured by Image software, which is much larger than 199 nm of pure carbon nanofiber. The surface of graphene/PANI nanocomposites, **Figure 2.2(h)** is rougher than that of pure graphene, **Figure 2.2(g)**. All the results indicate the PANI are coated on the surface of carbon nanomaterials.

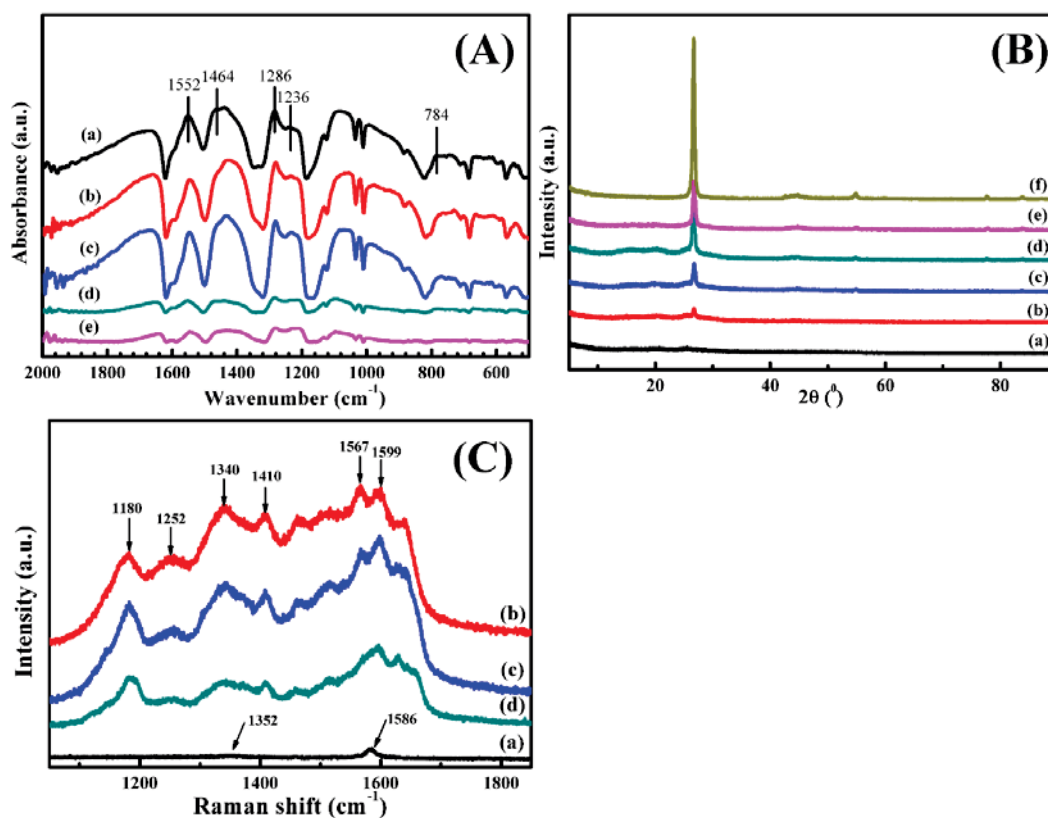


Figure 2.4 (A) FT-IR spectra of (a) pure PANI, and graphene/PANI nanocomposites with (b) 5.0, (c) 10.0, (d) 20.0, and (e) 40.0 wt% graphene; (B) XRD spectra of (a) PANI, (b) 5.0 wt% graphene/PANI, and (c) 10.0 wt% graphene/PANI, (d) 20.0 wt% graphene/PANI, (e) 40.0 wt% graphene/PANI, and (f) pure graphene nanoparticles; (C) Raman spectra of (a) graphene, (b) PANI, (c) 10.0 wt% graphene/PANI and (d) 40.0 wt% graphene/PANI nanocomposites.

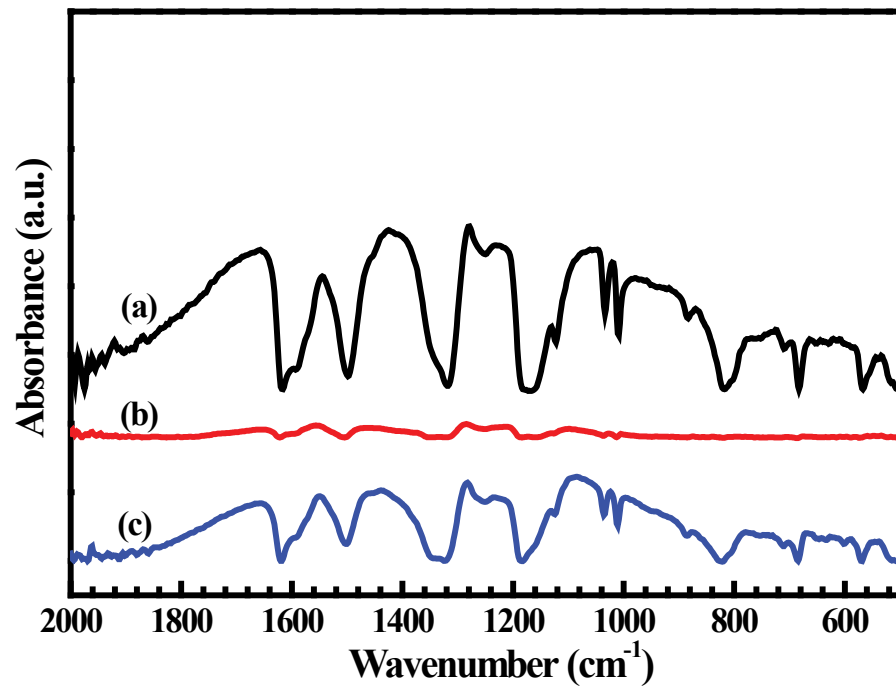


Figure 2.5 FT-IR spectra of (a) 10.0 wt% carbon black/PANI, (b) 10.0 wt% carbon nanotube/PANI and (c) 10.0 wt% carbon nanofiber/PANI nanocomposites.

2.3.2 FT-IR, Raman and X-ray diffraction analysis

Figure 2.4 shows the (A) FT-IR, (B) XRD and (C) Raman analysis of PANI and its nanocomposites. For the FT-IR spectrum of pure PANI, **Figure 2.4A(a)**, the peaks located at 1552 and 1464 cm^{-1} correspond to the characteristic C=C stretching vibration of the quinoid and benzenoid rings, respectively, indicating the oxidation state of emeraldine salt in the PANI.^{36, 37} The peak at 1286 cm^{-1} corresponds to the C-N stretching vibration of the benzenoid unit, and the peak located at 1236 cm^{-1} is attributed to the C-H in-plane vibration of the quinoid unit.³⁸ The peak at 784 cm^{-1} is due to the out-of-plane vibration of C-H in the substituted benzenoid ring.³⁵ All the characteristic peaks of PANI is consistent with previous FT-IR spectra analysis of PANI.³⁹ **Figure 2.4A(b-e)** shows FT-IR spectra of the PANI nanocomposites with different graphene loadings. The characteristic peaks of PANI are also observed in the graphene/PANI nanocomposites. Compared with pure PANI, the characteristic peaks of graphene/PANI nanocomposites have a shift about 4 to 19 cm^{-1} , indicating the interaction between graphene and PANI.³⁸ **Figure 2.5** shows the FT-IR spectra of 10.0 wt% carbon black/PANI, 10.0 wt% carbon nanotube/PANI and 10.0 wt% carbon nanofiber/PANI nanocomposites. The characteristic peaks of PANI are also obviously observed in these carbon based PANI nanocomposites. For 10.0 wt% carbon black/PANI nanocomposites, the characteristic peak located at 1545 cm^{-1} corresponds to the C=C stretching vibration of the quinoid rings, and the peak at 1460 cm^{-1} is due to the C=C stretching vibration of the benzenoid rings. The C-N stretching vibration of the benzenoid unit is reflected at 1279 cm^{-1} . The peak located at 1228 cm^{-1} is attributed to the C-H in-plane vibration of the quinoid unit, and the peak at 773 cm^{-1}

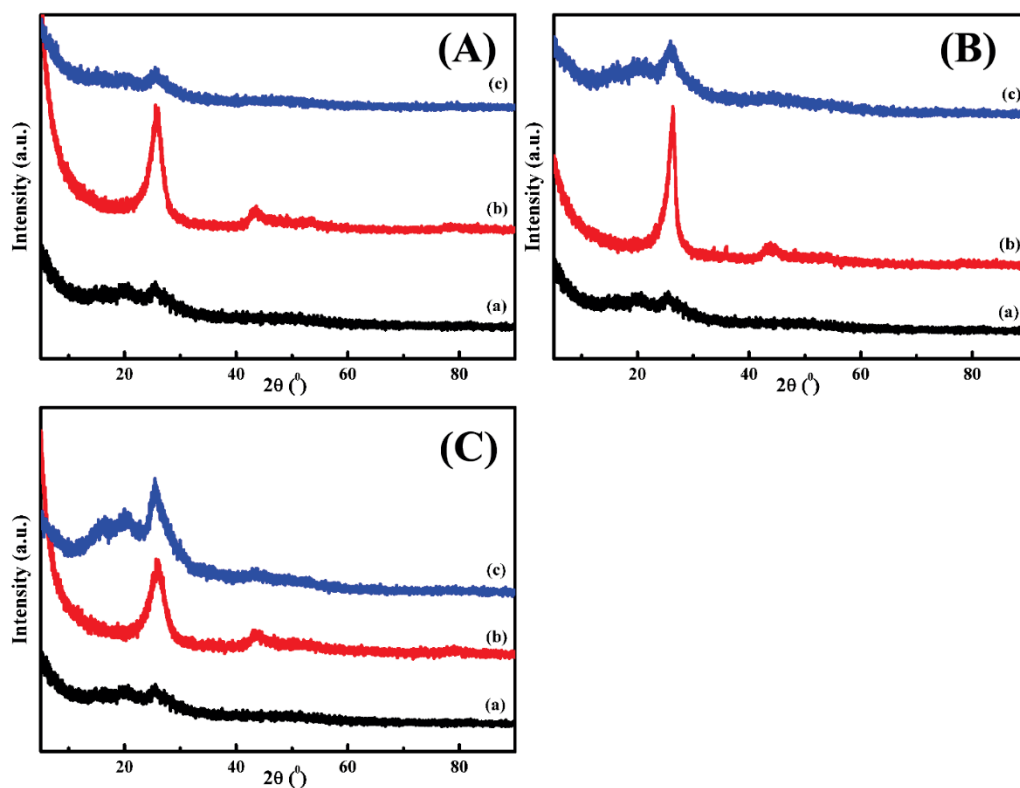


Figure 2.6 A): XRD patterns of a) PANI, b) carbon black, and c) 10.0 wt% carbon black/PANI nanocomposites; B): XRD patterns of a) PANI, b) carbon fiber, and c) 10.0 wt% carbon fiber/PANI nanocomposites; C): XRD spectra of a) PANI, b) carbon tube, and c) 10.0 wt% carbon tube/PANI nanocomposites.

corresponds to the out-of-plane vibration of C-H in the substituted benzenoid ring. These characteristic peaks have a shift compared with those of PANI, and the characteristic peaks of 10.0 wt% carbon nanotube/PANI and 10.0 wt% carbon nanofiber/PANI nanocomposites show the peak shifts as well. The shift of the peaks indicates the interaction between carbon nanoparticles and PANI, which results from the charger delocalization on the PANI.^{35, 38}

Figure 2.4B shows XRD patterns of pure PANI, graphene and graphene/PANI nanocomposites with 5.0, 10.0, 20.0 and 40.0 wt% graphene. For pure PANI, **Figure 2.4B(a)**, there are two broad peaks located at around 20.2 and 25.3° corresponding to the (100) and (110) crystallographic planes of partially crystalline PANI.⁴⁰ The peak located at 2θ of 26.66° appears in the pattern of pure graphene, **Figure 2.4B(f)**, which corresponds to the (002) planes of a graphitic structure with short-range order in some stacked graphene sheets.⁴¹ The characteristic peaks of both pure graphene and PANI are also observed in the graphene/PANI nanocomposites, **Figure 2.4B(b-e)**. The intensity of the diffraction peak of graphene increases with increasing the graphene loading in the graphene/PANI nanocomposites. The intensity of the diffraction peak of pure PANI decreases with increasing the graphene. **Figure 2.6** displays the XRD patterns of carbon black/PANI, fiber/PANI and tube/PANI nanocomposites with the 10.0 wt% nanofillers. In **Figure 2.6A(b)**, two amorphous peaks of carbon black centered at 25.5 and 43.6° are ascribed to the graphitic planes (002) and (101), respectively.^{42, 43} The peak located at 25.5° indicates the dominating of disordered carbon phase, and the peak at 43.6° indicates the existence of graphitic layers with smaller sizes and lower three-dimensional order.⁴² The characteristic peaks of carbon black are also observed in the nanocomposites, **Figure 2.6A(c)**. The two

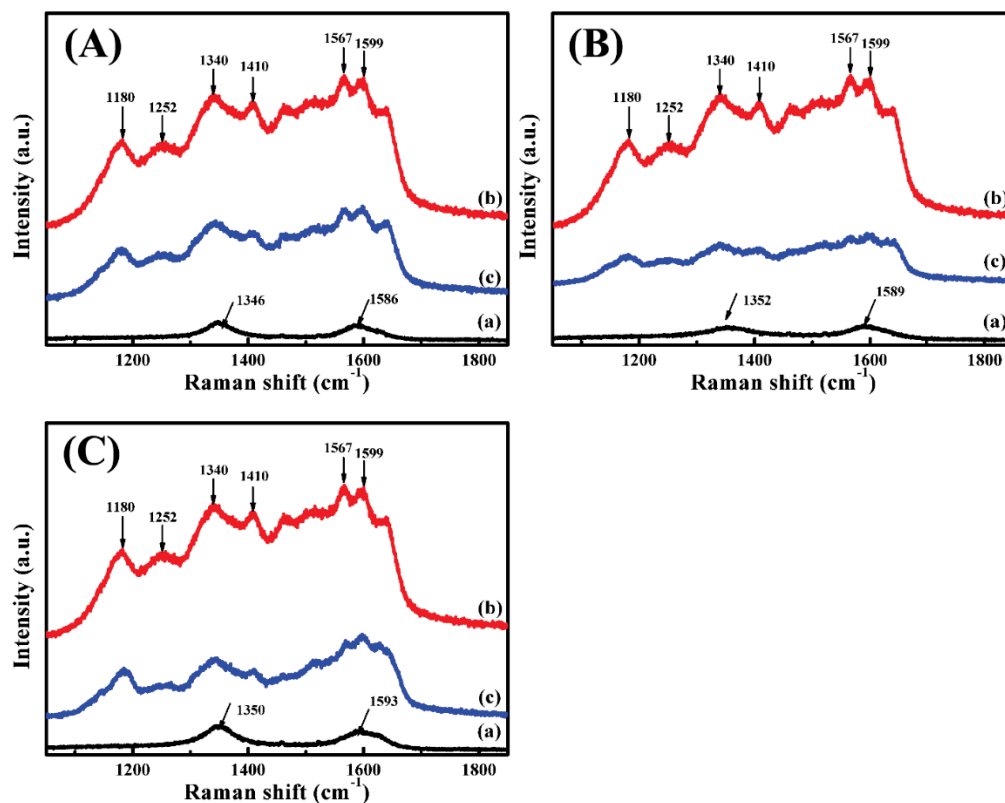


Figure 2.7 A): Raman spectra of a) carbon black, b) PANI, c) 10.0 wt% carbon black/PANI nanocomposites.; B): Raman spectra of a) carbon fiber, b) PANI, c) 10.0 wt% carbon fiber/PANI nanocomposites; C): Raman spectra of a) carbon tube, b) PANI, c) 10.0 wt% carbon tube/PANI nanocomposites.

board peaks of carbon fiber at 26.3 and 43.8° suggest the disorder graphitic (002) and (101) planes, **Figure 2.6B(b)**.⁴⁴ These characteristic peaks are also observed in the carbon fiber/PANI nanocomposites, **Figure 2.6B(c)**. For carbon nanotubes, **Figure 2.6C(b)**, the characteristic peaks located at 25.7 and 43.9° reflect the (002) and (101) planes.⁴⁰ These peaks are also observed in the carbon tube/PANI nanocomposites, **Figure 2.6C(c)**. The characteristic peaks of pure PANI and carbon nanomaterials are observed in the PANI nanocomposites, indicating the PANI/nanocomposites are synthesized successfully.

Raman spectroscopy was further used to study the chemical structure of graphene, PANI and graphene/PANI nanocomposites, **Figure 2.4C**. For pure graphene, **Figure 2.4C(a)**, the peaks centered at 1352 and 1586 cm⁻¹ correspond to D and G bands.⁴⁵ The E_{2g} phonon mode of in-plane sp² carbon atoms lead to the appearance of G band, and D band is due to the presence of sp³ defects within the graphene sheets.^{46, 47} The Raman spectrum of pure PANI, **Figure 2.4C(b)**, shows bands at 1180, 1252, 1340, 1410, 1567, and 1599 cm⁻¹ corresponding to the C-H in-plane bending, C-N in-plane stretching, C-N⁺ in-plane stretching of the bipolaron structure, N-H bending, C=C in-plane stretching, and C-C in-plane stretching of the benzenoid ring, respectively.^{31, 48, 49} The characteristic peaks of PANI were observed in the graphene/PANI nanocomposites. The characteristic peak of graphene at 1352 cm⁻¹ is located between characteristic peaks (1340 and 1567 cm⁻¹) of PANI; the other characteristic peak of graphene at 1586 cm⁻¹ is located between 1567 and 1599 cm⁻¹ of PANI. For PANI, the intensity of peak at 1567 cm⁻¹ is relatively stronger than that of peak at 1599 cm⁻¹. However, for 10.0 wt% graphene/PANI nanocomposites, **Figure 2.4C(c)**, as the existence peak of graphene 1586 cm⁻¹, the intensity of peak at 1567 cm⁻¹ is

relatively weaker than that of peak at 1599 cm^{-1} in the 10.0 wt% graphene/PANI nanocomposites. When the graphene loading increases to 40.0wt%, these two peaks become a one board peak in the 40.0 wt% graphene/PANI nanocomposites, **Figure 2.4C(d)**. Because of the peak of graphene at 1352 cm^{-1} , the peak of PANI at 1340 cm^{-1} for 40.0 wt% graphene nanocomposites becomes board in comparison with that of pure PANI. **Figure 2.7** shows the Raman spectra of carbon black/PANI, fiber/PANI and tube/PANI nanocomposites with 10.0 wt% nanofillers. The characteristic peaks of carbon black, carbon fiber and carbon tube are all located at around 1352 cm^{-1} for D bond, and 1586 cm^{-1} for G bond. The characteristic peaks of PANI and the carbon nanomaterials are all observed in the carbon based PANI nanocomposites.

2.3.3 Thermogravimetric analysis

Figure 2.8 shows the thermal stability of pure PANI and PANI nanocomposites with different carbon nanofillers in the air condition. For pure carbon nanomaterials, the pure graphene, **Figure 2.8a**, and carbon fiber, **Figure 2.8c**, display very good thermal stability, the weight loss of the pure graphene and carbon fiber are almost zero during the temperature range.^{50, 51} The onset weight loss temperature are 731.2 and $523.9\text{ }^{\circ}\text{C}$ for pure carbon black and carbon nanotube, **Figure 2.8(b&d)**, respectively. The main weight loss temperature range for carbon black is from 731.2 to $854.1\text{ }^{\circ}\text{C}$; the mass of carbon nanotube decreases sharply from to 523.9 to $624.1\text{ }^{\circ}\text{C}$. The $T_{-20\%}$ (the temperature at 20% mass loss) and $T_{-30\%}$ (the temperature at 30% mass loss) of carbon back are higher than that of carbon nanotube, hence the thermal stability of carbon fiber is better than carbon nanotube. For pure PANI, there are two weight loss regions observed, Figure 3. The weight loss from

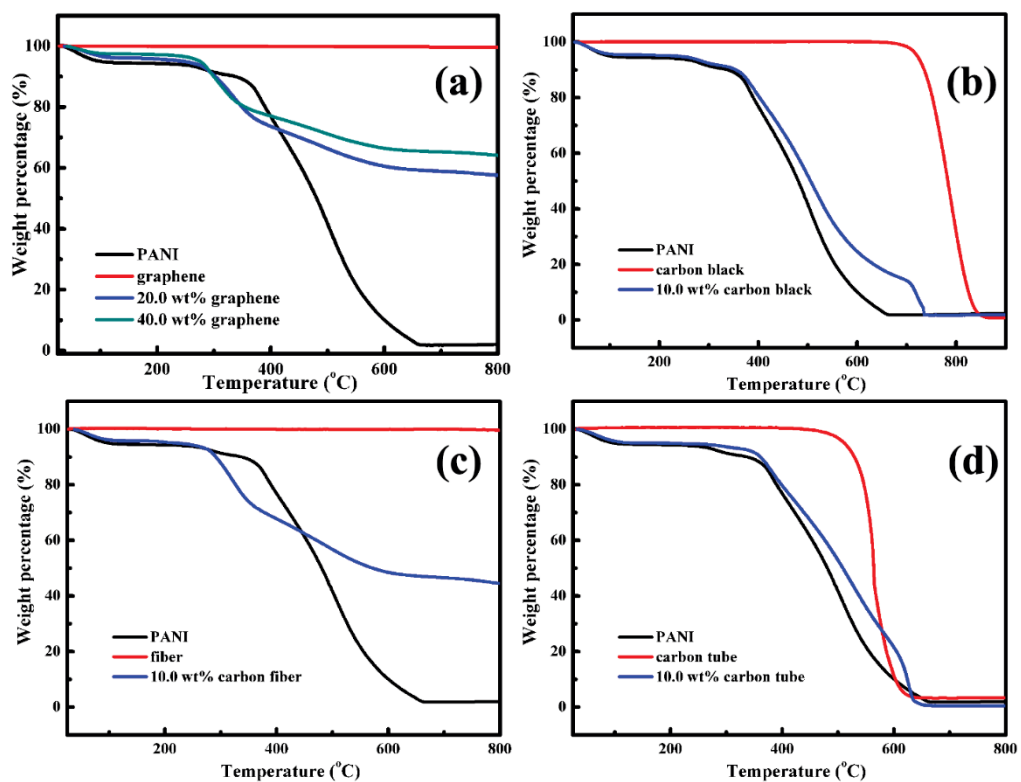


Figure 2.8 TGA curves of PANI nanocomposites with (a) graphene, (b) carbon black, (c) carbon fiber and (d) carbon tube in air condition.

Table 2.1 Thermal analysis of PANI and its nanocomposites under air atmosphere.

Sample	T _{onset} /°C	T _{-20%} /°C	T _{-30%} /°C
PANI	339.6	390.2	422.5
graphene	/	/	/
20.0 wt% graphene/PANI	276.3	349.3	450.4
40.0 wt% graphene/PANI	273.3	354.6	518.9
carbon black	731.2	752.2	764.0
10.0 wt% carbon black/PANI	342.5	402.7	441.7
carbon fiber	/	/	/
10.0 wt% carbon fiber/PANI	273.3	326.5	378.3
carbon tube	523.9	546.4	555.1
10.0 wt% carbon tube/PANI	345.3	398.9	439.2

room temperature to around 305 °C is attributed to the elimination of the moisture and decomposition of doped acid in the PANI sample.³⁵ The second weight loss from 305 to around 662 °C is for the degradation of PANI.⁵² The weight residue of PANI is about 2.0 % indicating the carbonization of PANI. For graphene/PANI nanocomposites, two weight loss stages are observed as well, **Figure 2.8a**. The T_{onset} of graphene nanocomposites is lower than that of pure PANI, indicating a relative lower thermal stability of the graphene nanocomposites. However, $T_{-30\%}$ of graphene nanocomposites is higher than that of pure PANI. The T_{onset} , $T_{-20\%}$ and $T_{-30\%}$ of all the samples are summarized in Table 1. The two weight loss stages are also observed in the carbon fiber/PANI nanocomposites in **Figure 2.8c**, and carbon nanotube/PANI nanocomposites in **Figure 2.8d**. However, there are three weight loss regions observed in the carbon black/PANI nanocomposites, **Figure 2.8b**. The first and second weight loss are due to the elimination of the moisture, decomposition of doped acid and degradation of PANI at different temperature ranges. The third weight loss stage from 699.8 to 734.6 °C is due to the degradation of the carbon black. The T_{onset} , $T_{-20\%}$ and $T_{-30\%}$ of carbon black/PANI nanocomposites are higher than pure PANI, carbon fiber/PANI and carbon nanotube/PANI at the same loading indicating carbon black/PANI nanocomposites exhibit an enhanced thermal stability. From all the above results, it is obvious that morphology, thermal stability and loading of the carbon nanomaterials affect the thermal stability of the PANI nanocomposites.

2.3.4 Dielectric property

Figure 2.9 displays the frequency dependences of real permittivity (ε'), imaginary permittivity (ε'') and dielectric loss tangent ($\text{Tan}\delta = \frac{\varepsilon''}{\varepsilon'}$) for pure PANI and its

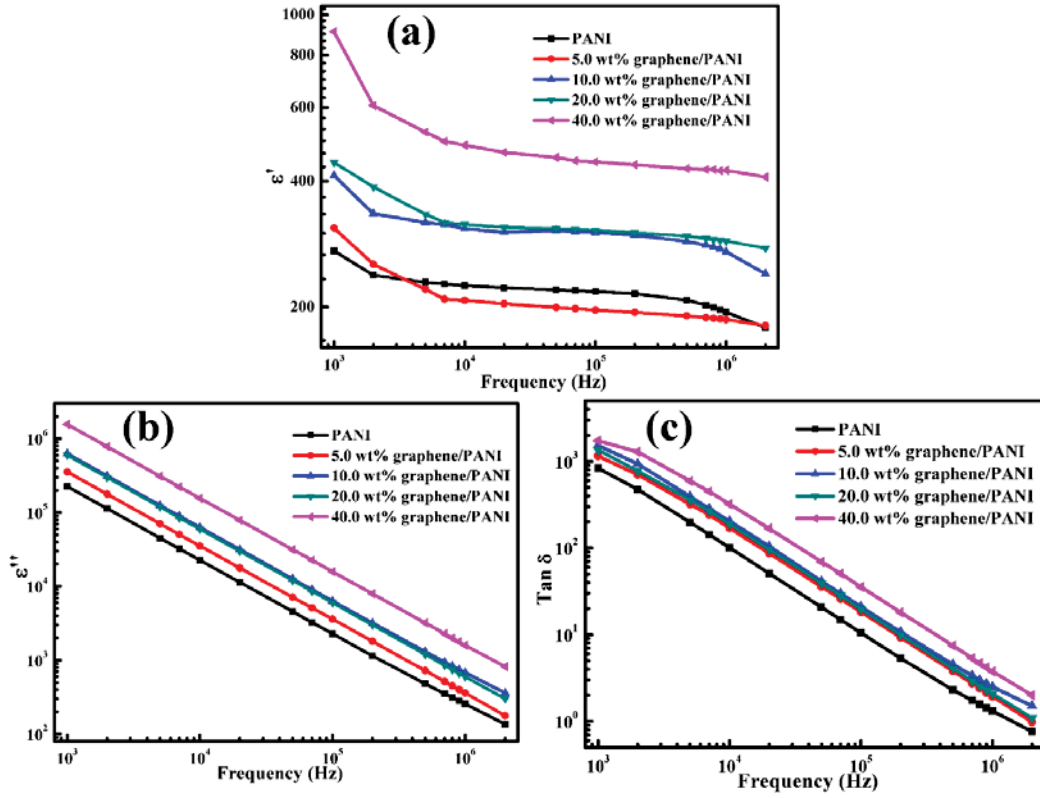


Figure 2.9 (a) real permittivity (ϵ'), (b) imaginary permittivity (ϵ''), and (c) dielectric loss ($\tan \delta$) as a function of frequency of pure PANI, graphene/PANI nanocomposites with a graphene loading of 5.0, 10.0, 20.0 and 40.0 wt%.

nanocomposites in a frequency range from 800 to 2×10^6 Hz at room temperature. All the samples show positive ε' in the measured frequency range. As conjugated polymer, the electrical behavior of PANI depends on its disorder, because PANI contains homogeneous and inhomogeneous parts.⁵³ Normally, the crystalline metallic regions (homogeneous part) are surrounded by amorphous barriers (inhomogeneous part), and the charge carriers could hop among the metallic regions overcoming the barriers.^{53, 54} The real permittivity ε' of PANI, **Figure 2.9a**, decreases with increasing the frequency in the measured frequency range. Generally, the ε' of dielectric medium decreases with increasing the frequency because of the electric leakage.⁵⁵ The ε' of PANI decreases sharply at low frequency, then shows a relative stability within the frequency range from 1×10^4 to 8×10^5 Hz. The ε' of PANI presents sharply decreasing at low frequency is due to the Maxwell–Wagner–Sillars polarization effect, in which the charge carriers are accumulated at the internal interfaces or at external electrode-sample interface on a macroscopic scale under the electrical field.²⁰ The ε' of PANI decreases at higher frequency. At high frequency, the polarization of charge carrier exhibits a “delay” with respect to a changing electric field, which is the well-known dielectric relaxation phenomena.⁵² The graphene/PANI nanocomposites with different graphene loadings show the same trend as pure PANI, and the ε' increases with increasing the graphene loading in the graphene nanocomposites. Due to the relatively lower graphene loading, the ε' of 5.0 wt% graphene/PANI nanocomposites did not show significantly increasing. Normally, the nanocomposites as dielectric medium can be regarded as a series of micro-capacitors.⁵⁵ For graphene/PANI nanocomposites, the appearance of graphene results to more interface areas, which lead to the formation of more equivalent

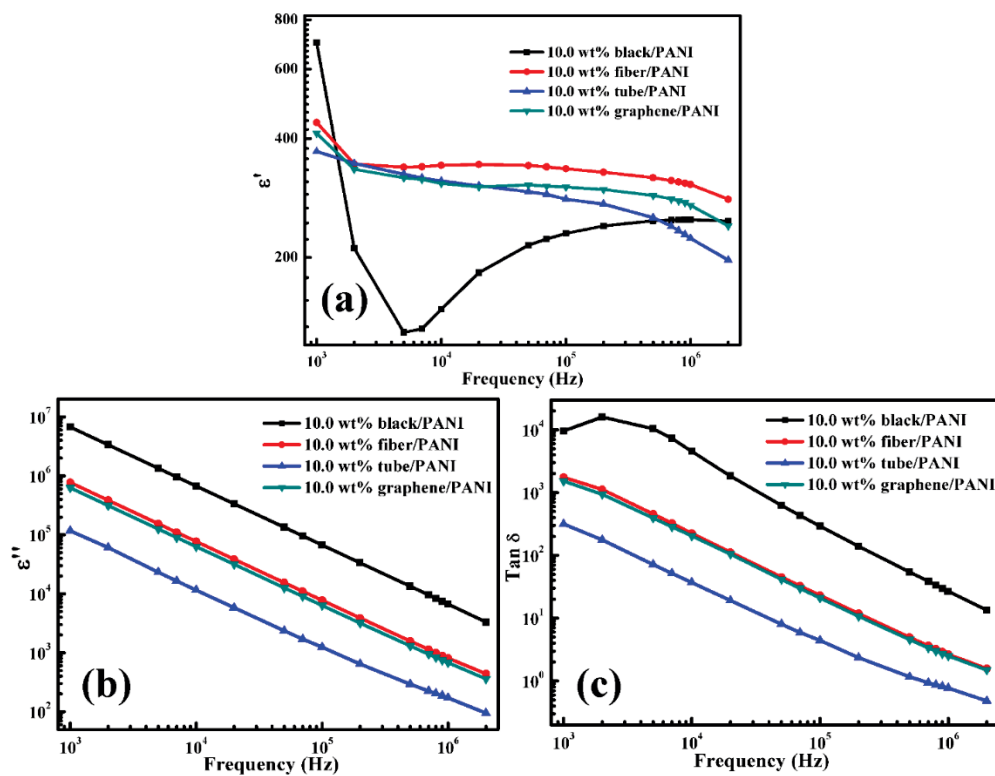


Figure 2.10 (a) ϵ' , (b) ϵ'' , and (c) $\tan \delta$ as a function of frequency of PANI nanocomposites with carbon black, carbon nanofiber, carbon nanotube and graphene at 10.0 wt% loading.

micro-capacitors in the composites. Therefore, higher permittivity appears with higher graphene loading in the graphene/PANI nanocomposites. **Figure 2.9(b&c)** shows the imaginary permittivity and dielectric loss tangent for pure PANI and its nanocomposites. Both ϵ'' and $\tan\delta$ of PANI and PANI nanocomposites are positive and decrease with increasing the frequency. The graphene/PANI nanocomposites show higher ϵ'' and $\tan\delta$ values than pure PANI, and ϵ'' and $\tan\delta$ values increase with increasing the graphene loading. Normally, the dielectric loss could be described by ϵ'' or $\tan\delta$. For PANI and its nanocomposites, the dielectric loss is mostly related to the frequency and the graphene loading; and the interfacial polarization loss and conduction loss lead to the dielectric loss.⁵⁵⁻⁵⁷ The dielectric loss of graphene/PANI nanocomposites increases with increasing the graphene loading which may be due to more conduction loss and interfacial loss.

Figure 2.10 exhibits ϵ' , ϵ'' and $\tan\delta$ for the PANI nanocomposites with different carbon nanomaterials in a frequency range from 800 to 2×10^6 Hz at room temperature. The ϵ' value of PANI nanocomposites with fiber, tube and graphene are larger than that of pure PANI and exhibit the same trends with increasing the frequency, **Figure 2.10a**. The ϵ' of carbon fiber/PANI nanocomposites is higher than those of PANI nanocomposites with other carbon nanofillers. The decreasing ϵ' is due to the Maxwell–Wagner–Sillars polarization effect and dielectric relaxation phenomena at different frequency range. It is interesting to observe that carbon black/PANI nanocomposites experience three different stages, **Figure 2.10a**. At the first stage, the ϵ' decreases with increasing the frequency from 10^3 to 5×10^3 Hz, then increases with increasing from 7×10^3 to 6×10^6 Hz at second stage, then slightly decreases with increasing the frequency at the third stage. The ϵ'' and

$\tan\delta$ decrease with increasing the frequency, **Figure 2.10(b&c)**. As discussed before, the dielectric loss is attribute to interfacial polarization loss and conduction loss. The carbon nanomaterials in the PANI nanocomposites lead to more conduction loss. Therefore, the PANI nanocomposites with carbon nanofillers shows higher dielectric loss. The decreasing dielectric loss with increasing the frequency is due to the reduced real permittivity.

2.3.5 Temperature dependent resistivity and electrical conduction mechanism

The temperature dependent resistivity of pure PANI and its carbon based nanocomposites with different loadings of carbon black, carbon fiber, carbon nanotube and graphene was measured from 135 to 290 K to determine the electrical conduction mechanism. In **Figure 2.11a**, the resistivity of pure PANI decreases from 85.86 to 14.8 ohm.cm within the temperature range. For the graphene/PANI nanocomposites, the resistivity of 10.0 wt% graphene/PANI nanocomposites decrease from 79.90 to 6.17 ohm.cm, when the particle loading was 40.0 wt% in the graphene/PANI nanocomposites, the resistivity decreases from 1.05 to 0.26 ohm.cm. the resistivity of pure PANI and graphene/PANI nanocomposites decrease with increasing the temperature, indicating a typical behavior of semiconductor, **Figure 2.11a**.⁵⁸ In the doped conductive polymer, the charge carriers on the polymer are localized. The localization prevents the electron conduction, because the doped acids (dopants) are partially ordered near polymer chains and the ionic charges could confine the electron randomly.⁵⁹ The thermal excitation is needed for the movement of the charge carrier from one site to the other site, hence the resistivity decreases as the temperature decreases.⁵⁹

The resistivity decreases with increasing the graphene loading in the graphene/PANI nanocomposites. The resistivity of PANI nanocomposites with carbon

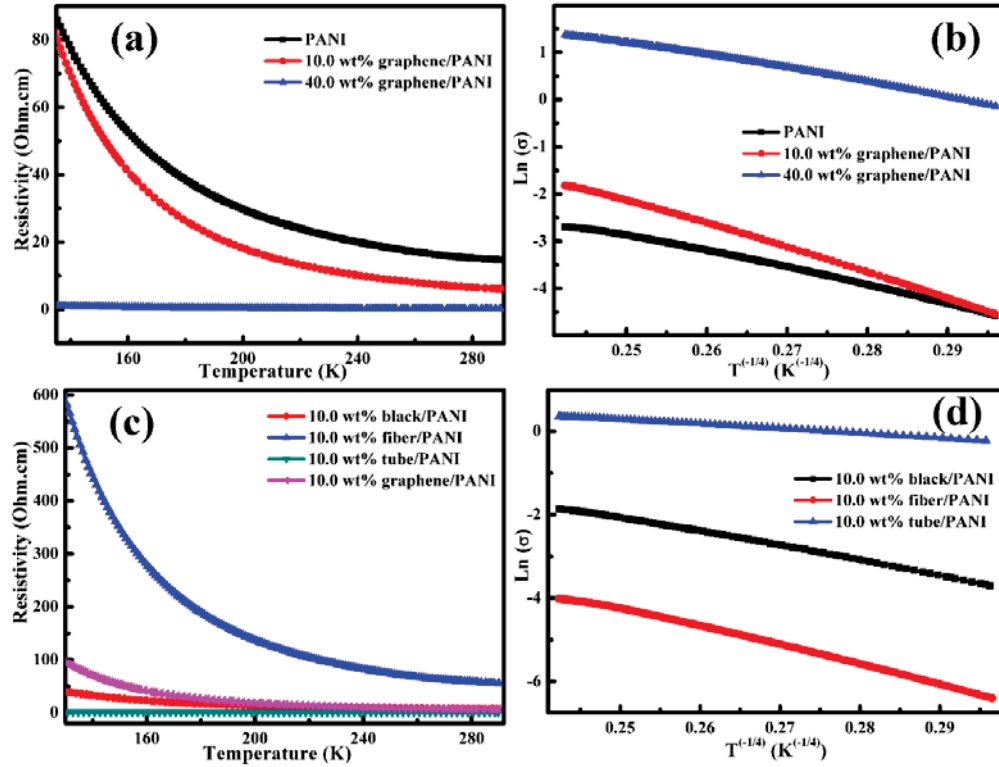


Figure 2.11 (a) Temperature dependent resistivity and (b) $\ln(\sigma)$ as a function of $T^{-1/4}$ of PANI and graphene/PANI nanocomposites; (c) Temperature dependent resistivity and (d) $\ln(\sigma)$ as a function of $T^{-1/4}$ of PANI nanocomposites with carbon black, fiber and tube, respectively.

black, carbon fiber and carbon nanotube, **Figure 2.11c**, also decrease with increasing the temperature and thus show a semiconductor behavior as well. For 10.0 wt% carbon black/PANI, carbon fiber/PANI, and carbon tube/PANI, the resistivity decreases from 35.56 to 6.43 ohm, 506.18 to 55.46 ohm.cm, and 1.22 to 0.70 ohm.cm within the measured temperature range, respectively. For the conjugated polymers such as PANI and polypyrrole, the electron behavior of conductive polymers depends on the amount of disorder which means the variations in conjugation length, rotations and kinking of polymer chain interactions with neighboring conjugated molecules, impurities and dipoles from residual solvent molecules.^{53, 60} The disorder can be expressed by the resistivity ratio (ρ_r , $\rho_r = \rho_{135} / \rho_{290}$).⁶¹ The calculated disorder for PANI and its nanocomposites is summarized in **Table 2.2**. It is interesting to find that the disorder of the PANI nanocomposites can be adjusted by the morphology of the nanofillers, but the electrical conductivity does not show the same trend as the change of the disorder. This maybe because the good electrical conductivity of the carbon nanofillers affect the electrical behavior of the charge carriers in the nanocomposites. The similar phenomenon was observed in the polypyrrole nanocomposites with different carbon nanostructures.³⁴

The VRH model is applied to describe the electrical conduction mechanism and could be expressed as equation 1:³⁵

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{1+n}} \right] \quad n=1, 2, 3 \quad (1)$$

The pre-exponential factor σ_0 , representing the conductivity at infinite low temperature limit, is a constant. The n value of 3, 2, and 1 stands for three-, two-, and one- dimensional

Table 2.2 ρ_r , σ_0 and T_0 for the pure PANI, and PANI nanocomposites with different carbon nanofillers.

Sample	ρ_r	σ_0 (S cm ⁻¹)	$T_0 \times 10^5$ (K)
Pure PANI	5.80	409.00	15.89
10 wt% black/PANI	5.53	654.3812	13.68
10 wt% fiber/PANI	9.13	979.4195	39.33
10 wt% tube/PANI	1.74	20.65567	0.14
10 wt%			
grapene/PANI	12.95	46229.81	70.10
40 wt%			
grapene/PANI	4.04	3741.268	6.19

systems, respectively. T is the Kelvin temperature (K) and T_0 is the hopping barrier standing for the characteristic Mott temperature (the energy needed for charge carriers hopping conduction) and is described as equation 2:¹⁷

$$T_0 = 24 / [\pi k_B N(E_F) a_0^3] \quad (2)$$

where k_B is Boltzmann constant, the $N(E_F)$ is the density of states at the fermi level, and a_0 is the localization length.⁶²

The equation 1 can be rearranged to equation 3:

$$\ln \sigma = \ln \sigma_0 - \left(\frac{T_0}{T} \right)^{1/n} \quad n=1, 2, 3 \quad (3)$$

Thus, σ_0 and T_0 can be obtained from the intercept and slope of the plot $\ln(\sigma) \sim T^{-1/(1+n)}$, respectively. The obtained results from temperature dependent resistivity, **Figure 2.11(a&c)** are shown in **Figure 2.11(b&d)**. All the synthesized samples are observed to follow $\ln(\sigma) \sim T^{-1/4}$ linear relationship, indicating a quasi 3-dimensional VRH mechanism. Therefore, the dimension of the carbon nanofiller does not affect the electrical conduction mechanism of the PANI. The calculated σ_0 and T_0 are summarized in **Table 2.2**. Generally, a larger T_0 indicates a stronger localization accompanied by an increased resistivity.⁶³ The calculated σ_0 did not show the same change trend as the disorder, however, the calculated T_0 shows the same change trend as the disorder for the PANI and PANI nanocomposites.

2.3.6 Magnetoresistance

The magnetic field dependent resistivity of PANI and its carbon based nanocomposites at room temperature is shown in **Figure 2.12**. For all the synthesized

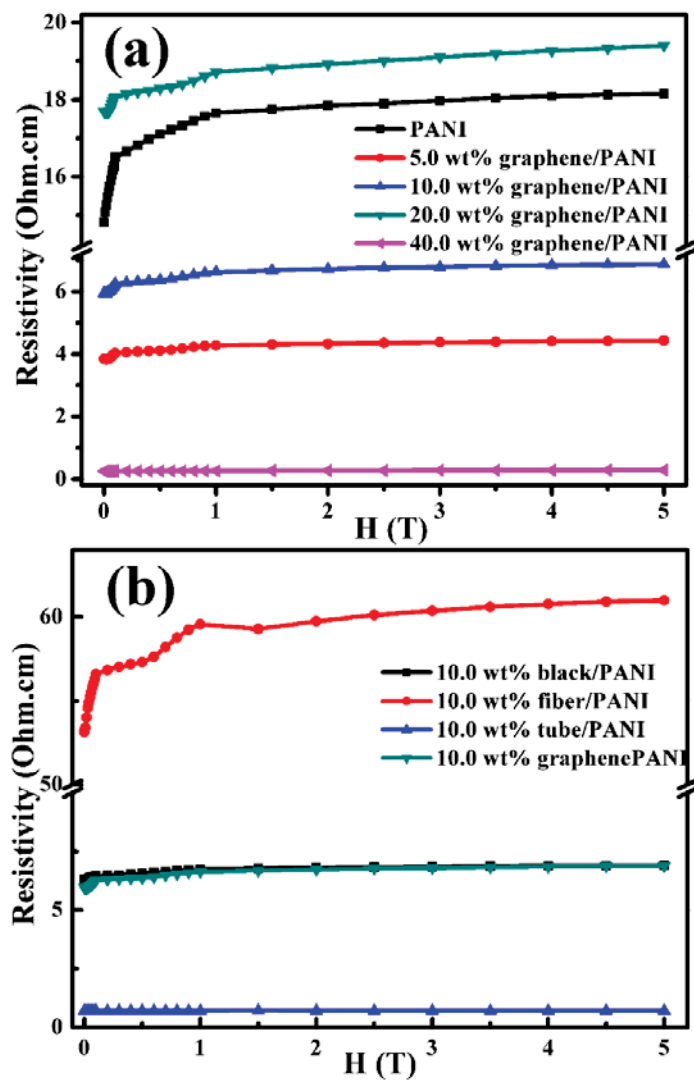


Figure 2.12 Magnetic field dependent Resistivity of a) graphene/PANI nanocomposites, b) PANI nanocomposites with carbon black, fiber and tube, respectively.

samples, the resistivity increases with increasing the magnetic field, which show the opposite trend as the temperature dependent resistivity. For the PANI nanocomposites with different carbon nanomaterials, **Figure 2.12(b)**, the fiber/PANI nanocomposites show a higher resistivity in the magnetic field range. At low magnetic field, the linear relationship between resistivity and magnetic field is observed, the ratio of resistivity to magnetic field is higher, indicating a higher sensitivity to the change of the magnetic field. These results indicate that the charge carrier behavior under the temperature and magnetic field is affected by different factors. For the conjugated polymers, its conductivity is based on the electron transport hopping mechanism.⁵⁴ The resistivity decreases with increasing the temperature is due to the thermal excitation. But the increasing resistivity with increasing the magnetic field is different.

The charge carrier behavior under the magnetic field is studied by the MR phenomenon. And MR is expressed as equation 4:⁶⁴

$$\text{MR}\% = \frac{R(H) - R(0)}{R(0)} \times 100 \quad (4)$$

where $R(0)$ is the resistance when magnetic field is 0 T, and $R(H)$ is the resistance under the magnetic field H . The room temperature MR values of PANI and its nanocomposites with different carbon nanomaterials are displayed in **Figure 2.13 and 2.14**, and all the samples shows the positive MR. The MR value of graphene/PANI nanocomposites is lower than that the pure PANI. The MR decreases when the graphene loading increases from 5 to 20 wt%, then increases when the graphene loading reaches 40 wt%, **Figure 2.13a**. It is interesting to find that the MR increases with increasing the particle loading for the PANI nanocomposites with 1-dimensional carbon nanofiber and nanotube, **Figure 2. 14(b&c)**,

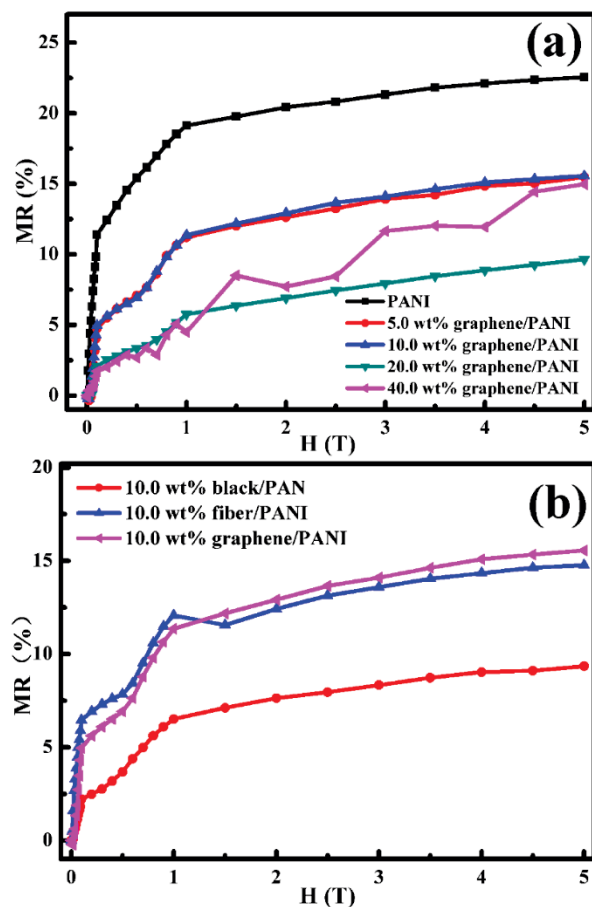


Figure 2.13 Room temperature MR of (a) PANI and its nanocomposites with graphene and (b) PANI nanocomposites with carbon black, carbon fiber, and graphene.

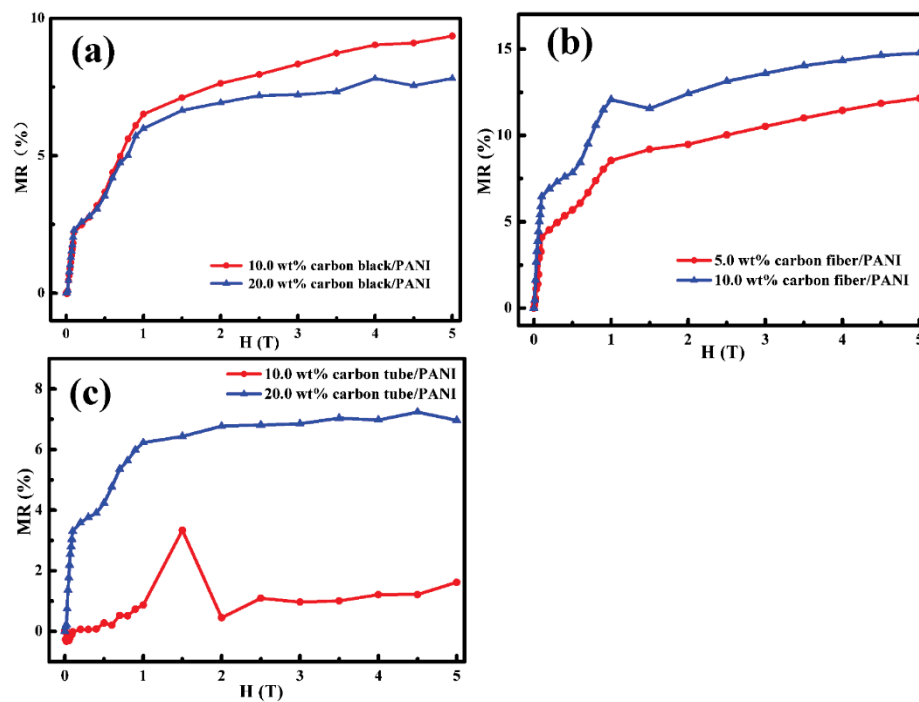


Figure 2.14 Room temperature MR of PANI nanocomposites with a) carbon black, b) carbon fiber and c) carbon tube.

but it decreases with increasing the particle loadings for the PANI with carbon black, **Figure 2.14(a)**. The PANI nanocomposites with the 10.0 wt% carbon nanomaterials are shown in **Figure 2.14b**. The MR value decreases from graphene/PANI to fiber/PANI, then from carbon black/PANI to carbon nanotube/PANI nanocomposites. All the above results indicate that the dimension of the carbon nanomaterials and loading affects the MR behavior of the conjugated PANI.

In recent years, researchers have paid much attention to the MR behavior of organic systems. Until now, many models have been developed to study electron hopping behavior in the organic semiconductors, including excitonic pair mechanism model,⁶⁵ electron-hole recombination model,⁶⁶ bipolaron model,⁶⁷ forward interference model¹⁷ and wave-function shrinkage model.⁵⁴ Generally, the orbital magnetoconductivity theory (forward interference model) and wave-function shrinkage model can be used to describe the MR of highly disorderedly localized systems in the VRH regime. In the temperature dependent resistivity section, pure PANI and its nanocomposites with different carbon nanomaterials exhibit 3-*d* Mott VRH electrical conduction mechanism, indicating that the electron behavior obeys the VRH model. Hence, the wave-function shrinkage model is used to study the charge carrier behavior under the magnetic field. In the wave-function shrinkage model, once the magnetic field applied to conductive polymer, the shape of the wave function of the doped electron (or impurity electron) would be changed, which leads to the overlap area between the neighboring wave function of the electron become smaller, then the hopping probability for the electron is reduced. Eventually, the resistivity is increased and the positive MR is observed in the conductive polymers.⁵⁴ Therefore, this model is

designed to study the positive MR of the conductive polymers. The $R(H,T)/R(0,T)$ can be expressed as equation 5:⁵⁴

$$R(H,T)/R(0,T) = \exp\{L_c(0)[L_c(H)/L(0) - 1]\} \quad (5)$$

where $L_c(0) = (T_0/T)^{1/4}$ for the 3-*d* Mott VRH charge transport mechanism, $L_c(H)/L_c(0)$ is the normalized hopping probability parameter and is a function of H/P_C for the Mott VRH charge transport mechanism, H is the magnetic field, P_C is the fitting parameter, which is the normalizing characteristic field that must be extracted from one set of MR ratio data points and can also be given by equation 6 for the Mott VRH charge transport mechanism:^{30, 54}

$$P_C = 6\hbar/[ea_0^2(T_0/T)^{1/4}] \quad (6)$$

where e is electron charge, $\hbar$ is the reduced Planck's constant. In the low magnetic field limit, equation 5 is simplified to equation 7:³⁰

$$R(H,T)/R(0,T) \approx 1 + t_2 \frac{H^2}{P_C^2} \left(\frac{T_0}{T}\right)^{1/4} \quad (7)$$

The MR is defined as equation 4, for the Mott VRH model, the MR can be expressed as equation 8:

$$\text{MR} = \frac{R(H,T) - R(0,T)}{R(0,T)} = t_2 \frac{e^2 a_0^4}{36\hbar^2} \left(\frac{T_0}{T}\right)^{3/4} H^2 \quad (8)$$

where the numerical constant t_2 is 5/2016, it's obviously observed that MR value in equation 8 is always positive, hence, the wave-function shrinkage model will always be positive and used to explain the positive MR value. According to equation 8, the a_0 can be calculated from equation 9:

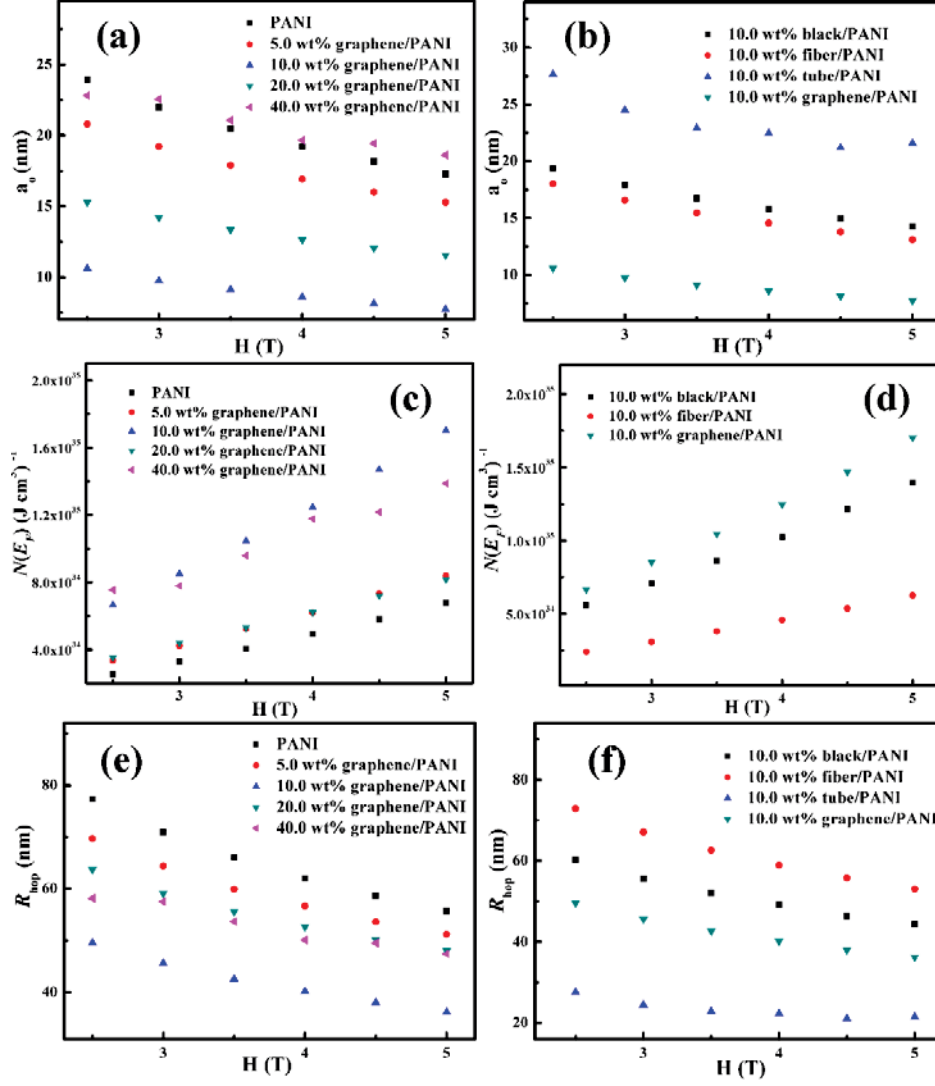


Figure 2.15 (a) localization length, (c) density of state at fermi level, (e) average hopping length of pure PANI and graphene/PANI nanocomposites; (b) localization length, (d) density of state at fermi level, (e) average hopping length of PANI nanocomposites with different carbon nanofillers at 10.0 wt% loading.

$$a_0^4 = \frac{36\hbar^2 MR}{t_2 e^2} \left(\frac{T_0}{T}\right)^{-3/4} H^{-2} \quad (9)$$

The a_0 as a function of the magnetic field is shown in **Figure 2. 15 (a&b)**. It is obvious that a_0 of all the synthesized samples decrease with increasing the magnetic field strength. Because with increasing the strength of the magnetic field, the deformation of the wave function of the electron becomes larger. As we mentioned in the temperature dependent resistivity part, the resistivity ratio shows the same trend as T_0 for the PANI and its nanocomposites. Normally, a higher resistivity ratio, a stronger disorder; a larger T_0 , a stronger localization. The calculated resistivity ratio and T_0 of the PANI and its graphene nanocomposites from high to low are 10.0 wt% > 20.0wt% > 5.0 wt% > PANI > 40.0 wt% graphene/PANI nanocomposites. For different carbon nanomaterials at the 10.0 wt% in the PANI nanocomposites, the resistivity ratio and T_0 from high to low is graphene/PANI > fiber/PANI > black/PANI > tube/PANI. In **Figure 2.15 (a&b)**, the value of the a_0 shows the opposite trend as the resistivity ratio and T_0 for PANI and its nanocomposites. Therefore, the localization is related to the disorder degree of the conjugated polymers; as the disorder becomes stronger, the localization becomes stronger, meanwhile the localization length becomes smaller.⁶⁸ It is interesting to find that the resistivity of the PANI and its nanocomposites did not show the same relation as disorder (resistivity from higher to low), because the conductivity of the carbon nanomaterials and loading are different. In a word, the carbon nanomaterials could adjust the disorder degree, conductivity, localization of the PANI matrix.

According to equation 10, the density of states at the fermi level $N(E_F)$ can be calculated after we got the localization length:³⁸

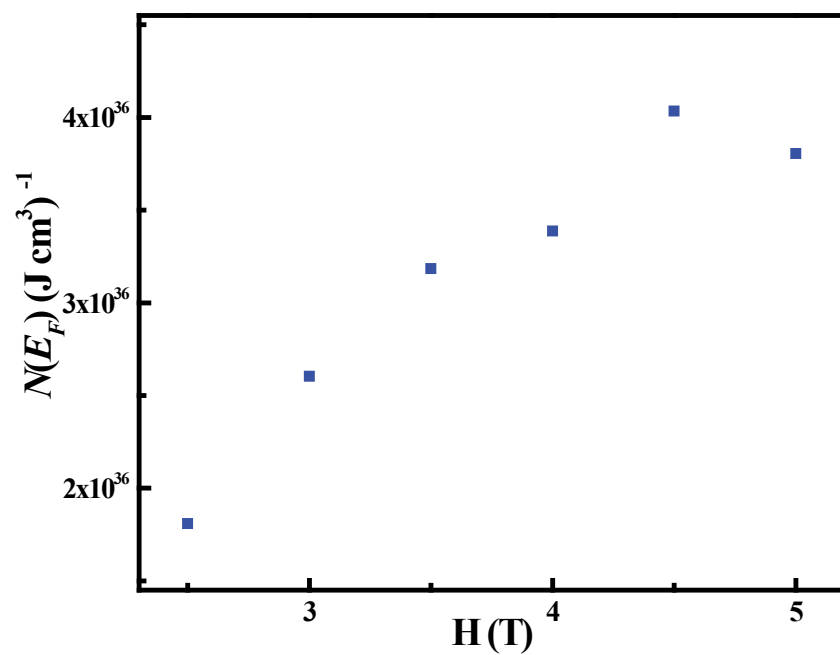


Figure 2.16 Density of state at fermi level for 10.0 wt% tube/PANI nanocomposites.

$$N(E_F) = 24/[\pi k_B T_0 a_0^3] \quad (10)$$

The obtained $N(E_F)$ for the PANI and its carbon nanomaterials are displayed in **Figure 2.15(c&d)** and **Figure 2.16**. The $N(E_F)$ decreases with increasing the magnetic field for all the synthesized samples. Generally, a relatively lower density of state at fermi level indicates a higher possibility for the existence of charge carrier delocalization.⁶⁹ For the PANI and its nanocomposites, the density of state at fermi level increases with increasing the strength of magnetic field, indicating a decreasing possibility of delocalization. Therefore, the positive MR is observed under the magnetic field. The $N(E_F)$ of graphene/PANI nanocomposites is higher than that of PANI.

The average hopping length R_{hop} can be obtained from equation 11 by T_0 , T and a_0 .³⁸

$$R_{hop} = (3/8)(T_0/T)^{1/4} a_0 \quad (11)$$

The obtained R_{hop} is shown in **Figure 2.15(e&f)**. These results indicate that the R_{hop} decreases with increasing the H and the increased MR accompanies with the reduced R_{hop} . The R_{hop} under the magnetic field of pure PANI is higher than that of the carbon based PANI nanocomposite. With the existence of the conductive carbon nanomaterials in the PANI nanocomposites, the charge carriers would hop from the PANI to the carbon materials or from carbon materials to PANI. Hence, the R_{hop} of PANI nanocomposites is lower than that of pure PANI.

The average hopping energy (W) could be expressed as equation 12:

$$W = \frac{3}{4\pi R_{hop}^3 N(E_F)} = \frac{3}{4\pi \left(\frac{3}{8}\right)^3 \left(\frac{T_0}{T}\right)^{3/4} a_0^3 \frac{24}{\pi k_B T_0 a_0^3}} = \frac{16T^{3/4} k_B T_0^{1/4}}{27} \quad (12)$$

It is very interesting to find that as both T and K_B are constant, the W is only a function of T_0 , indicating that the Magnetic field has no effect on the W . This discovery proves that the force induced by the magnetic field does not contribute work to the electrons and just changes the moving direction of the electrons. This explained why the shape of the wave function of the doped electrons is changed once the magnetic field applied.

2.4 Conclusion

The characteristic analysis of FT-IR, XRD, SEM, and Raman indicate that the PANI nanocomposites with 0, 1 and 2 dimensional carbon nanofillers were successfully synthesized by the SIP method. The thermal stability and loading of the carbon nanomaterials affect the thermal stability of the PANI nanocomposites. Enhanced thermal stability was observed in the carbon black/PANI nanocomposites. Increased dielectric constant was achieved in the PANI nanocomposites with the carbon nanofillers, which means that these nanocomposites show higher energy storage property, and have a potential for EMI shielding application.⁷⁰ The resistivity of PANI nanocomposites decreases with increasing the temperature, as observed in typical semiconductors. However, under the magnetic field, the resistivity increases with increasing the magnetic field strength. The quasi 3-d electron conduction mechanism was observed in PANI and its nanocomposites through the Mott VRH model, indicating that the dimension of the carbon nanofillers did not affect the charge transport mechanism. The wave functional shrinkage model was applied to study the positive MR of the PANI nanocomposites. The localization length, average hopping length and hopping energy decrease with increasing the magnetic field, however, the density of state at fermi level increases with increasing the magnetic field.

More importantly, the MR signal of the conductive polymer could be adjusted with the assistance of the carbon nanofillers. This research provides basic study work about the magnetic field, carbon nanofillers, and nanofiller's morphology effects on the electron conduction mechanism of the PANI nanocomposites, which has significant influence on the magnetic sensor design or information storage based on MR phenomenon.

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Chapter 3. Magnetoresistance of Magnetic Polyaniline Nanocomposites

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Abstract

The polyaniline (PANI) nanocomposites with different magnetic nanoparticles (Fe@C, Fe₃O₄ or CoFe₂O₄) have been successfully synthesized by using a facile surface initiated polymerization (SIP) method. The scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to study the surface morphology of PANI nanocomposites and nanoparticle dispersion within the polymer matrix. The chemical structure of the PANI nanocomposites were characterized by Fourier transform infrared (FT-IR) spectroscopy. The thermal stability of the magnetic PANI nanocomposites were assessed by thermogravimetric analysis (TGA). Temperature dependent resistivity indicated a quasi 3-dimensional variable range hopping (VRH) electrical conduction mechanism for the magnetic PANI nanocomposites. The positive magnetoresistance (MR) was observed in the synthesized PANI and magnetic PANI nanocomposites at room temperature and analyzed by the wave-function shrinkage model. The magnetic and dielectric properties of the magnetic PANI nanocomposites were studied in this work as well.

3.1 Introduction

Polymer nanocomposites are synthesized by dispersing different functional nanofillers into the polymer matrix. Due to the unique physiochemical properties arising from the combined characteristics of parent constituents into a single material, Polymer nanocomposites have attracted great interests.¹ Conductive polymer nanocomposites have been extensively investigated because of their potential applications in light emitting devices, batteries, electromagnetic interface shielding,¹ telecoms, electronics, fire retardants, biosensors, electrodes for electrodeposition and corrosion resistant coatings.² Among the conductive polymers such as polyaniline (PANI), polythiophene, poly(DNTD) and polypyrrole, PANI has attained much more attentions due to its low cost, easy preparation, high yield, controllable electrical conductivity and environmental stability.³ PANI has been widely used as gas sensors, biosensors, electrode materials, coupling agent and corrosion inhibitors.³⁻⁶ In recent years, the new applications of PANI and its nanocomposites were developed by the researchers such as electrochromic windows and information storage.^{7, 8}

Magnetoresistance (MR) is a phenomenon that reflects the resistance change of the materials under the applied magnetic field. Since the development of thin film technology in 1970s, the MR was discovered in the coupled multilayers of Fe/Cr in 1988.^{9, 10} Generally, the MR is classified to giant magnetoresistance (GMR), anisotropic magnetoresistance (AMR), tunnel magnetoresistance (TMR) and etc. recently, there are many works on the MR of PANI nanocomposites. Bin *et al.* reported the negative MR (-7.5%) in the PANI coated carbon fabrics nanocomposites.¹¹ Guo *et al.* reported the negative MR (-42%) of

TiO₂/PANI nanocomposites and the temperature effect on the MR behavior.¹² Gu *et al.* found the positive MR in the silicon/PANI nanocomposites.⁸ and positive MR (95%) in the magnetite/PANI nanocomposites with negative dielectric constant.¹³ However, there is less work about the MR behavior of PANI nanocomposites with different magnetic nanoparticles.

In this work, Fe@C/PANI, CoFe₂O₄/PANI and Fe₃O₄/PANI nanocomposites were synthesized using the surface initiated polymerization (SIP) method. The Fourier transform infrared (FT-IR) spectroscopy was used to characterize the chemical structure of the pure PANI and magnetic PANI nanocomposites. The thermal stability of the magnetic PANI nanocomposites was performed by thermogravimetric analysis (TGA). Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to depict the dispersion and morphology of the as-received Fe₃O₄, Fe@C, CoFe₂O₄, pure PANI and magnetic PANI nanocomposites. The frequency dependent permittivity, temperature dependent resistivity, MR, and magnetic properties are systematically investigated.

3.2 Experimental

3.2.1 Materials

The Fe@C, Fe₃O₄, and CoFe₂O₄, were obtained from Nanostructured & Amorphous Materials, Inc. The ammonium persulfate (APS, (NH₄)₂S₂O₈, 98%) and *p*-toluene sulfonic acid (PTSA, C₇H₈O₃S, ≥ 98.5%) and Aniline (C₆H₇N) were purchased from fisher scientific. All the chemicals were used as-received without any further treatment.

3.2.2 Fabrication of PANI nanocomposites with magnetic nanoparticles

The magnetic (Fe@C, Fe₃O₄ or CoFe₂O₄)/PANI nanocomposites were fabricated using the SIP method. Firstly, the magnetic Nanoparticles were dispersed in the aqueous solution containing PTSA (30 mmol) and APS (18 mmol) in 200 mL deionized water treated by 60 minutes sonication and mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) in an ice-water bath. Secondly, the aniline solution (36 mmol, 50 mL deionized water) was mixed with the magnetic nanomaterials suspension, and mechanically and ultrasonically stirred continuously for additional 120 minutes in the ice-water bath for polymerization. Thirdly, the product was vacuum filtered and washed with deionized water several times to remove any unreacted PTSA and APS, then washed with ammonia solution to dedope the PANI nanocomposites, then redoped with 1 M PTSA solution. The final synthesized nanocomposites were dried at 50 °C in oven overnight. The Fe@C/PANI nanocomposites with a Fe@C loading of 10.0, 20.0, 40.0 and 60.0 wt% were fabricated, Fe₃O₄/PANI nanocomposites with a Fe₃O₄ loading of 20.0, and 40.0% were synthesized, and CoFe₂O₄/PANI nanocomposites with a CoFe₂O₄ loading of 20.0 and 40.0 wt% were synthesized. Pure PANI was fabricated following the above procedures without adding any nanoparticles for comparison.

3.2.3 Characterizations

The morphologies of the as-synthesized materials were examined by a FEI Helios NanoLab 600i scanning electron microscopy (SEM, Hillsboro, OR). All the samples were sputter coated with a thin layer of carbon (about 3 nm) to ensure good imaging. The FT-IR spectra of the products were obtained on a Nicolet IS 10 (in the range from 650 to 2000

cm⁻¹ at a resolution of 4 cm⁻¹). The XRD was measured by D/max-rB wide-angle X-ray diffractometer at a Cu k_{α} wavelength of 0.154 nm. The scanning rate is 4 ° min⁻¹ from 10 to 80°. TGA was performed using TA Instrument TGA 2950 under air-flow rate of 60 mL min⁻¹ from 30 to 1000 °C with a heating rate of 20 °C/ min. Dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of 20 to 2×10^6 Hz at room temperature. The pure PANI and magnetic/PANI nanocomposites were pressed in a form of disc pellet with a diameter of 25 mm by a hydraulic presser. The same samples were also used to measure the resistivity and MR. The temperature dependent resistivity was measured by a standard four-probe method from 50 to 290 K. The MR measurement of the PANI nanocomposites were carried out using a standard four-probe technique by a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design at 290 K. The magnetic properties were also investigated in the 9-T PPMS by Quantum Design.

3.3 Results and discussions

3.3.1 Microstructure characterization

Figure 3.1 displays the morphologies of pure magnetic nanoparticles and magnetic/PANI nanocomposites. The shape of the Fe@C nanoparticle is sphere-like, **Figure 3.1a**. The surface of CoFe₂O₄ is smooth, **Figure 3.1b**, and the Fe₃O₄ shows the cubic shape, **Figure 3.1c**. The surface of all the pure magnetic nanoparticles are smooth. However, after treated by the conductive PANI, the surface of the PANI nanocomposites become rough, which indicates the PANI were coated on the surface of the nanoparticles. It is interesting to find that the morphologies of the magnetic/PANI nanocomposites are

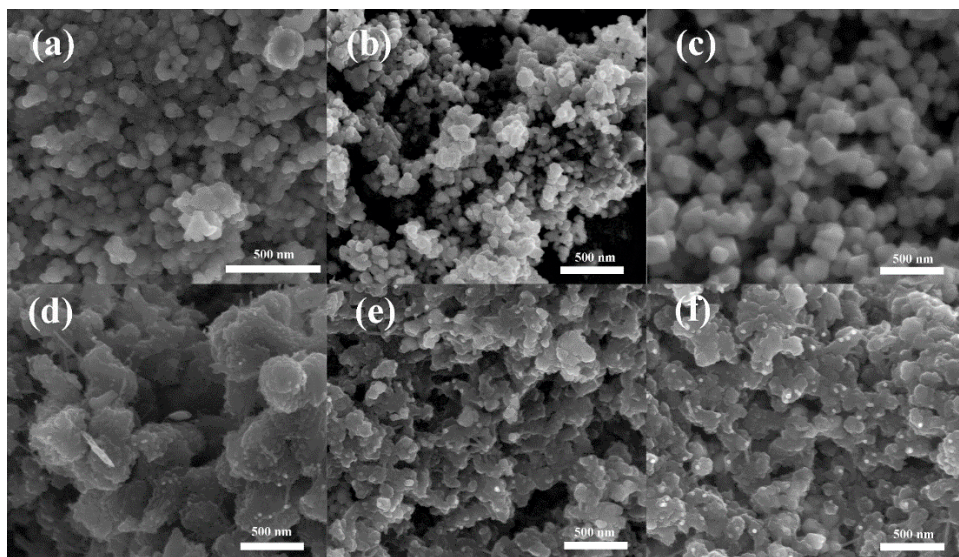


Figure 3.1 SEM images of (a) Fe@C, (b) CoFe₂O₄, (c) Fe₃O₄, (d) Fe@C/PANI, (e) CoFe₂O₄/PANI and (f) Fe₃O₄/PANI.

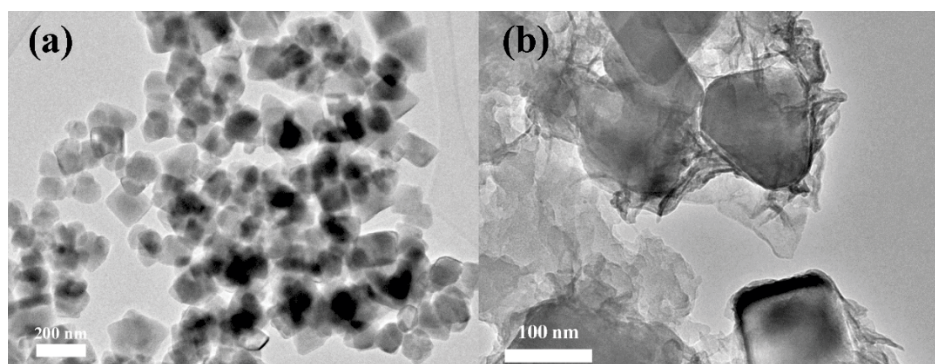


Figure 3.2 TEM images of (a) Fe₃O₄ and (b) Fe₃O₄/PANI.

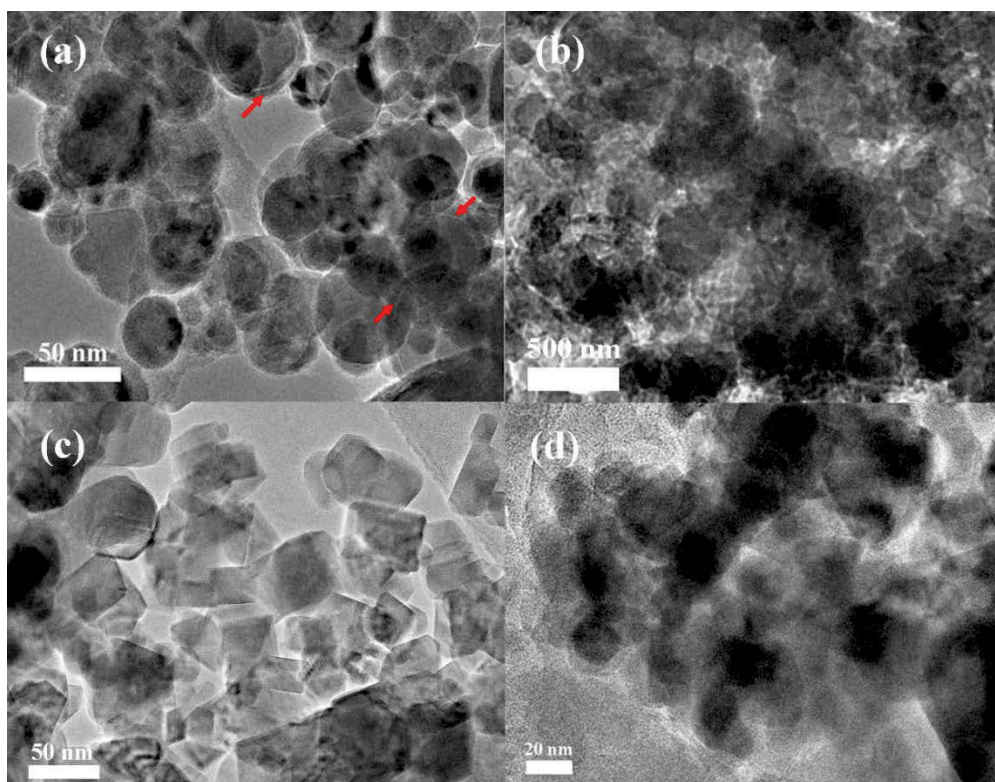


Figure 3.3 TEM images of (a) Fe@C, (b) CoFe₂O₄, (c) Fe@C/PANI and (d) CoFe₂O₄/PANI.

relative different, which may be due to the shape of the magnetic particles are different.

Figure 3.2 shows the TEM images of pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposites. It is obvious that the conductive PANI is coated on the surface of the Fe_3O_4 . In **Figure 3.3a**, the iron core carbon shell structure is observed in the pure Fe@C nanoparticles. The carbon shell is marked by the red arrows. The PANI coated Fe@C and CoFe_2O_4 nanocomposites are also observed in **Figure 3.3(b&d)**. All the above results indicate the magnetic PANI nanocomposites are successfully synthesized by the SIP method.

3.3.2 X-ray diffraction analysis

Figure 3.4 displays the XRD patterns of the pure magnetic nanoparticles and magnetic PANI nanocomposites with the same particle loading. There are 6 characteristic peaks observed in the pure Fe_3O_4 . The peaks located at $2\theta = 35.7, 43.3, 53.7, 57.2, 63.3$ and 74.3° in the XRD curve of Fe_3O_4 correspond to (311), (400), (422), (511), (400) and (533) crystallographic planes of the spinel phase of Fe_3O_4 , respectively.¹⁴ The characteristic peaks of Fe_3O_4 are also observed in the $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposites. For pure CoFe_2O_4 , the peaks located at $35.5, 37.1, 43.1, 53.1, 57.1$, and 62.7° correspond to (311), (222), (400), (422), (511), and (440) crystallographic planes of CoFe_2O_4 . All the observed characteristic peaks were indexed to the face-centered-cubic crystal structure of CoFe_2O_4 .¹⁵ The $\text{CoFe}_2\text{O}_4/\text{PANI}$ shows the characteristic peaks of pure CoFe_2O_4 as well. The characteristic peaks of Fe@C were also observed in the $\text{Fe@C}/\text{PANI}$ nanocomposites. All the observed results indicate that the magnetic PANI nanocomposites were successfully synthesized.

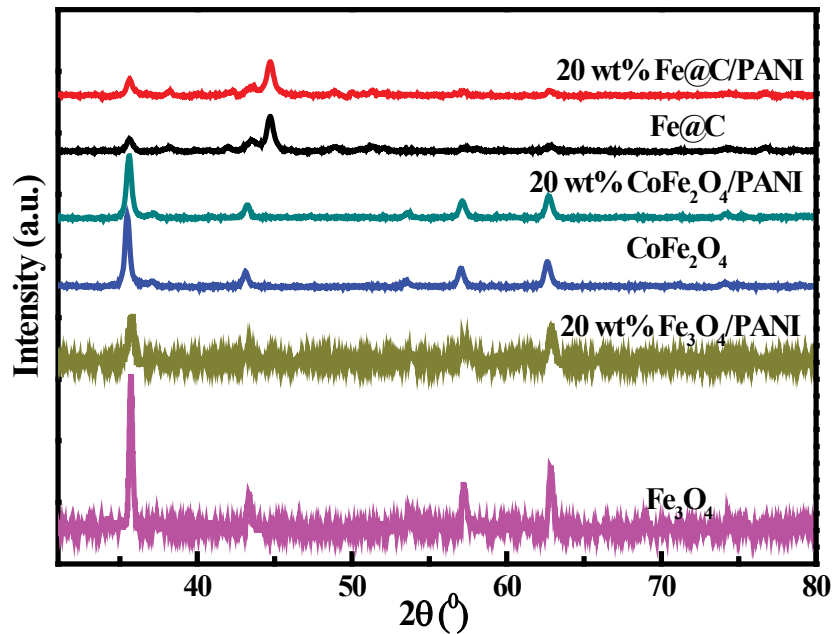


Figure 3.4 images of the XRD patterns of magnetic nanoparticles and the magnetic PANI nanocomposites.

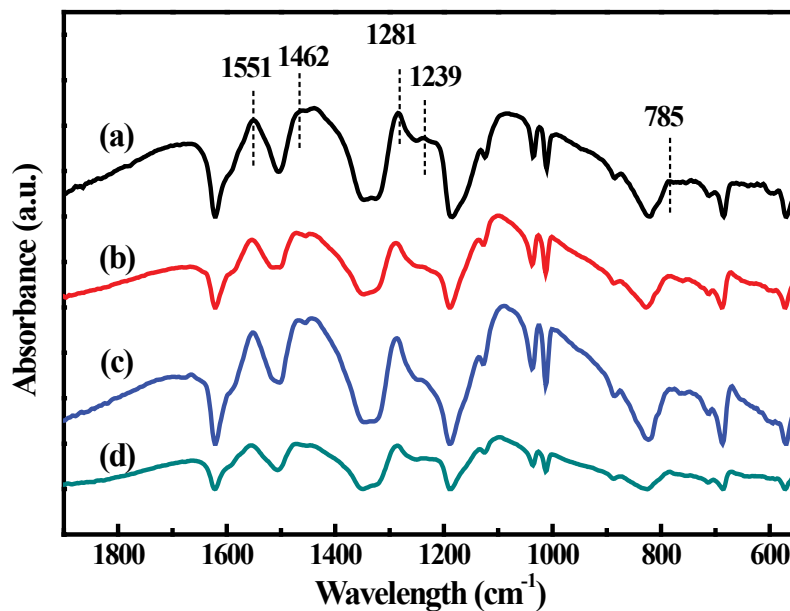


Figure 3.5 FT-IR spectra of (a) PANI, (b) 20 wt% Fe₃O₄/PANI, (c) 20 wt% CoFe₂O₄/PANI and (d) 20% FE@C/PANI.

3.3.3 FT-IR

Figure 3.5 shows the FT-IR spectra of pure PANI and magnetic PANI nanocomposites with different magnetic nanoparticles. For pure PANI, **Figure 3.5(a)**, the peak located at 785 cm^{-1} is due to the out of plane vibration of C-H in the substituted benzenoid ring.¹⁶ The peak at 1239 cm^{-1} is attribute to the C-H in-plane vibration of the quinoid unit.¹⁶ And the peak at 1281 cm^{-1} corresponds to the C-N stretching vibration of the benzenoid unit.¹⁷ The peaks located at 1551 and 1462 cm^{-1} correspond to the characteristic C=C stretching vibration of the quinoid and benzenoid rings, which indicate the oxidation state of emeraldine slat sate in the PANI.¹² For the magnetic PANI nanocomposites, **Figure 3.5(b, c & d)**, the characteristic peaks of PANI are observed in the PANI nanocomposites, which indicates that the PANI is successfully coated on the surface of the nanoparticles. However, compared with pure PANI, the characteristic peaks of magnetic PANI nanocomposites has a little shift, which indicates the interaction between the polymer and the magnetic nanoparticles.

3.3.4 Thermogravimetric analysis

Figure 3.6 shows the TGA curves of the pure PANI, Fe_3O_4 , CoFe_2O_4 , Fe@C and the magnetic PANI nanocomposites. There are two weight loss stages observed in the pure PANI. The first weight loss stage from room temperature to about $340\text{ }^\circ\text{C}$ is due to the elimination of moisture and doped PTSA in PANI.¹⁸ The second weight loss stage is degradation of the PANI chains from 340 to $665\text{ }^\circ\text{C}$.¹² The weight residue of pure PANI is 2.7% , which indicates that the PANI cannot get completely decomposed in air even at high temperature.¹¹ For the pure magnetic nanoparticles, the weight of Fe_3O_4 and CoFe_2O_4 is

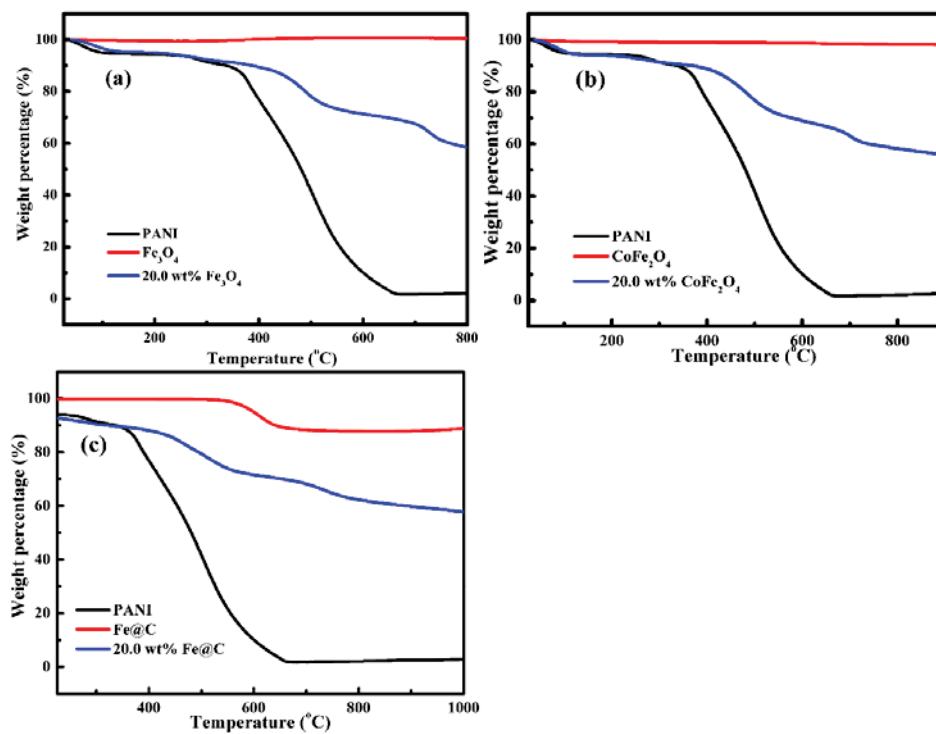


Figure 3.6 TGA curves of (a) 20 wt% Fe_3O_4 /PANI, (b) 20 wt% CoFe_2O_4 /PANI and (c) 40% $\text{Fe}@C$ /PANI.

almost no change, however, the as-received Fe@C shows a little weight loss. For the weight loss at 20 wt%, the magnetic PANI nanocomposites show higher temperature than that of pure PANI, indicating that the enhanced thermal stability of the magnetic PANI nanocomposites.

3.3.5 Dielectric property

Figure 3.7 shows the real permittivity ε' of pure PANI and magnetic PANI nanocomposites at room temperature. All the magnetic PANI samples shows positive ε' , and the ε' of PANI nanocomposites are higher than that of pure PANI, which is due to the interface areas formed between polymer and the magnetic nanoparticles.^{14, 19} For the Fe₃O₄/PANI nanocomposites, **Figure 3.7(a)**, the ε' increases with increasing the Fe₃O₄ nanoparticle loading, and decreases with increasing the frequency. However, for the CoFe₂O₄/PANI nanocomposites, **Figure 3.7(b)**, the 20 wt% CoFe₂O₄/PANI shows higher ε' than that of 40 wt% CoFe₂O₄/PANI nanocomposites. For the Fe@C/PANI nanocomposites, **Figure 3.7(c)**, it is interesting to observe that from 1×10^3 to 2×10^4 Hz, the ε' of 20 wt% Fe@C/PANI is higher than that of 40 wt% Fe@C/PANI nanocomposites, then ε' of 20 wt% Fe@C/PANI is lower than that of 40 wt% Fe@C/PANI nanocomposites with increasing the frequency.

Figure 3.8 shows the imaginary permittivity ε'' for pure PANI and magnetic PANI nanocomposites. The ε'' could be used to describe the dielectric loss. The ε'' of magnetic PANI nanocomposites are positive and decrease with increasing the frequency. The pure PANI shows relative lower ε'' than that of Fe₃O₄/PANI nanocomposites, and the ε'' increases with increasing the nanoparticle loadings, **Figure 3.8(a)**. For the CoFe₂O₄/PANI

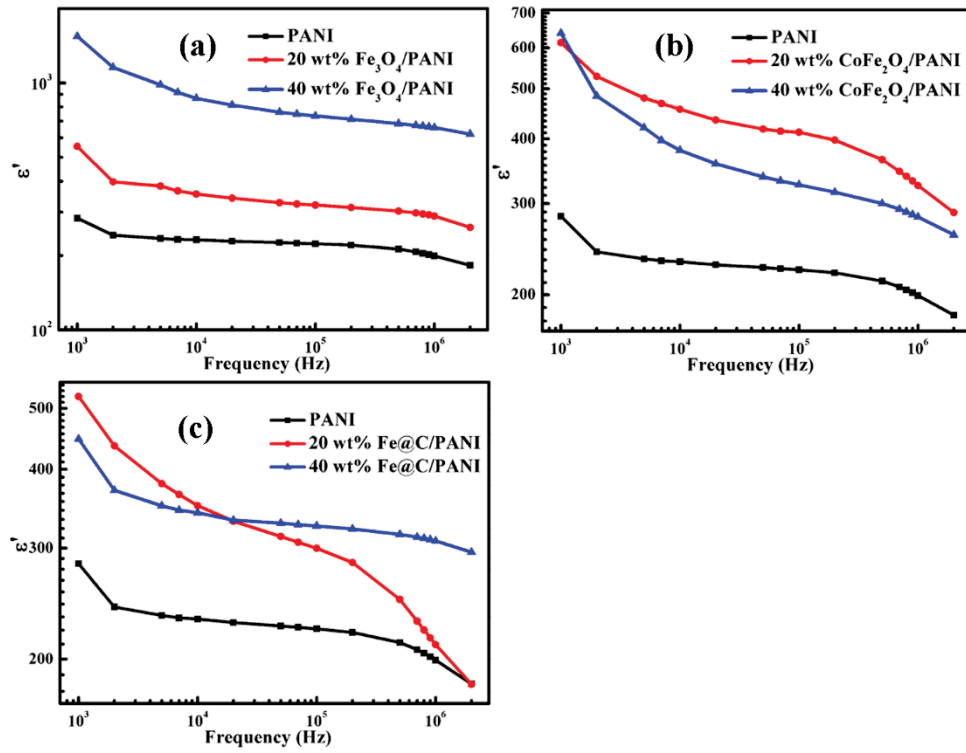


Figure 3.7 Real permittivity of (a) $\text{Fe}_3\text{O}_4/\text{PANI}$, (b) $\text{CoFe}_2\text{O}_4/\text{PANI}$ and (c) $\text{Fe@C}/\text{PANI}$ nanocomposites.

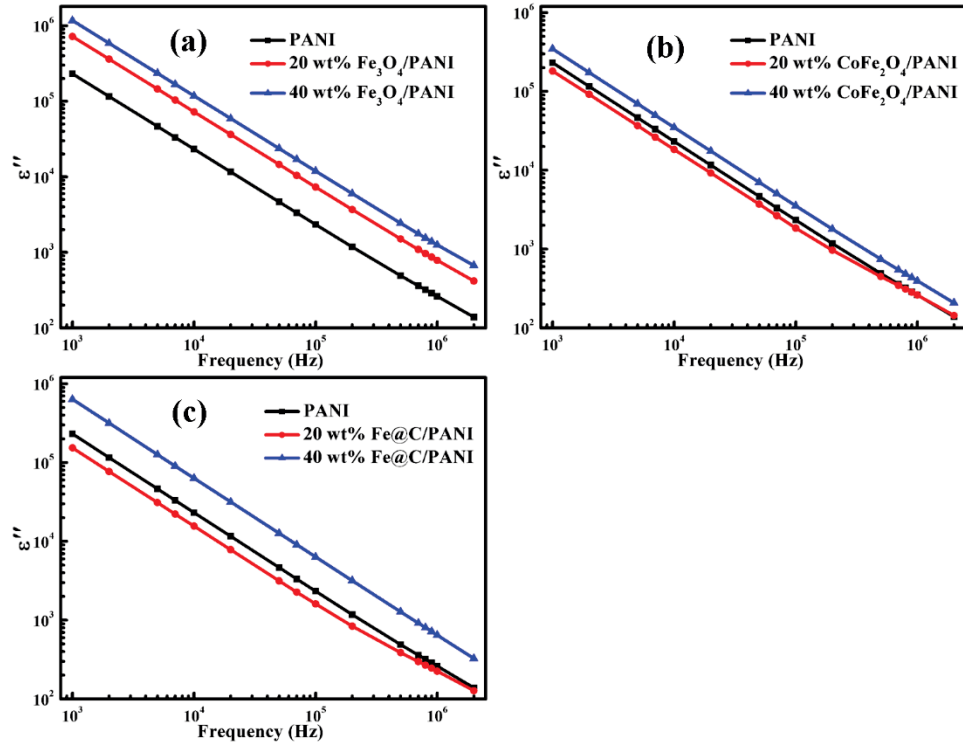


Figure 3.8 Imaginary permittivity of (a) $\text{Fe}_3\text{O}_4/\text{PANI}$, (b) $\text{CoFe}_2\text{O}_4/\text{PANI}$ and (c) $\text{Fe@C}/\text{PANI}$ nanocomposites.

nanocomposites, when the CoFe_2O_4 loading is 20 wt%, its ε'' is lower than that of pure PANI, and when the nanoparticle loading increases to 40 wt%, the ε'' is higher than that of pure PANI, **Figure 3.8(b)**. For the Fe@C/PANI nanocomposites, **Figure 3.8(c)**, the ε'' shows the same trend as $\text{CoFe}_2\text{O}_4/\text{PANI}$ nanocomposites. For the PANI nanocomposites, the conduction loss and interfacial polarization loss lead to the dielectric loss.²⁰⁻²²

3.3.6 Temperature dependent resistivity and electrical conduction mechanism

The temperature dependent resistivity of pure PANI and its nanocomposites with different magnetic nanoparticles were measured from 150 to 290 K to determine the electrical conduction mechanism. In **Figure 3.9(a)**, the resistivity of pure PANI and the Fe@C/PANI nanocomposites decrease with increasing the temperature, indicating a typical behavior of semiconductor.²³ The resistivity of the Fe@C/PANI nanocomposites increases with increasing the nanoparticle loading, so the nanoparticle loading affects the conductivity, and the doping degree could affect the conductivity as well.²⁴ All the Fe@C/PANI nanocomposites show higher resistivity than that of pure PANI. The resistivity of pure PANI decreases from 63.8 to 14.8 ohm.cm within the measured temperature range. The resistivity of Fe@C/PANI nanocomposites with different Fe@C loading varies from 9557.8 to 18.3 ohm.cm from 150 to 290 K. For $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposites, **Figure 3.9(b)**, the resistivity increases with increasing the nanoparticle loading. For the $\text{CoFe}_2\text{O}_4/\text{PANI}$ nanocomposites, **Figure 3.9(c)**, the resistivity increases with increasing the nanoparticle loading as well. The resistivity of $\text{CoFe}_2\text{O}_4/\text{PANI}$ nanocomposites is higher than that of $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposites at the same nanoparticle loading level.

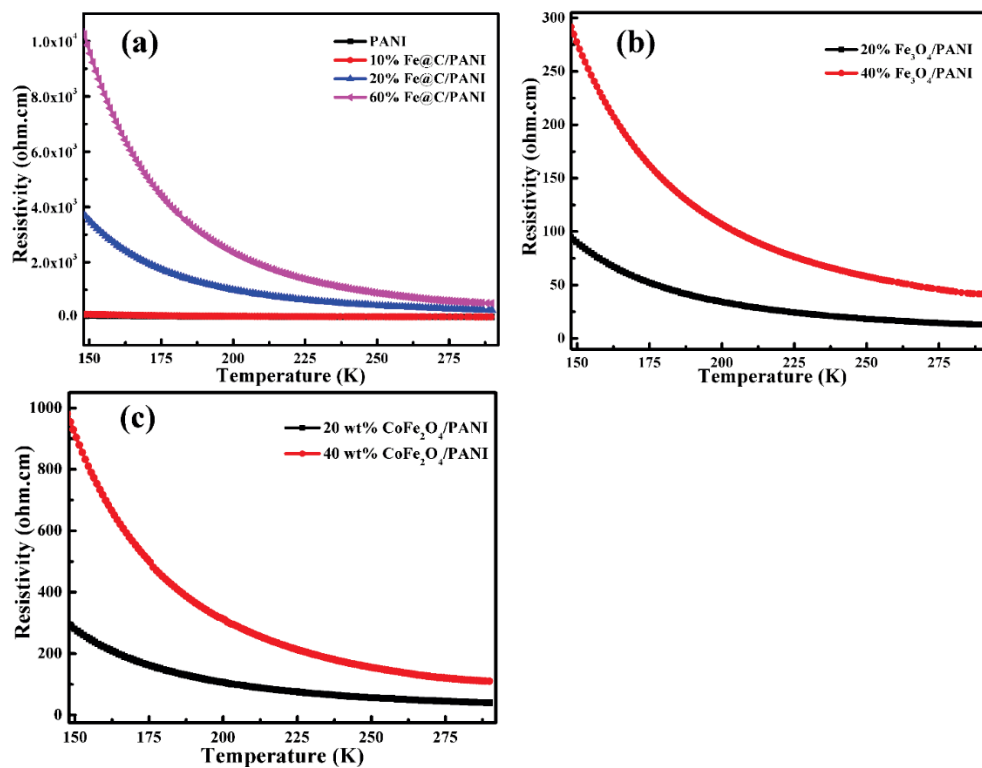


Figure 3.9 Temperature dependent resistivity of (a) pure PANI and Fe@C/PANI, (b) Fe₃O₄/PANI and (c) CoFe₂O₄/PANI nanocomposites.

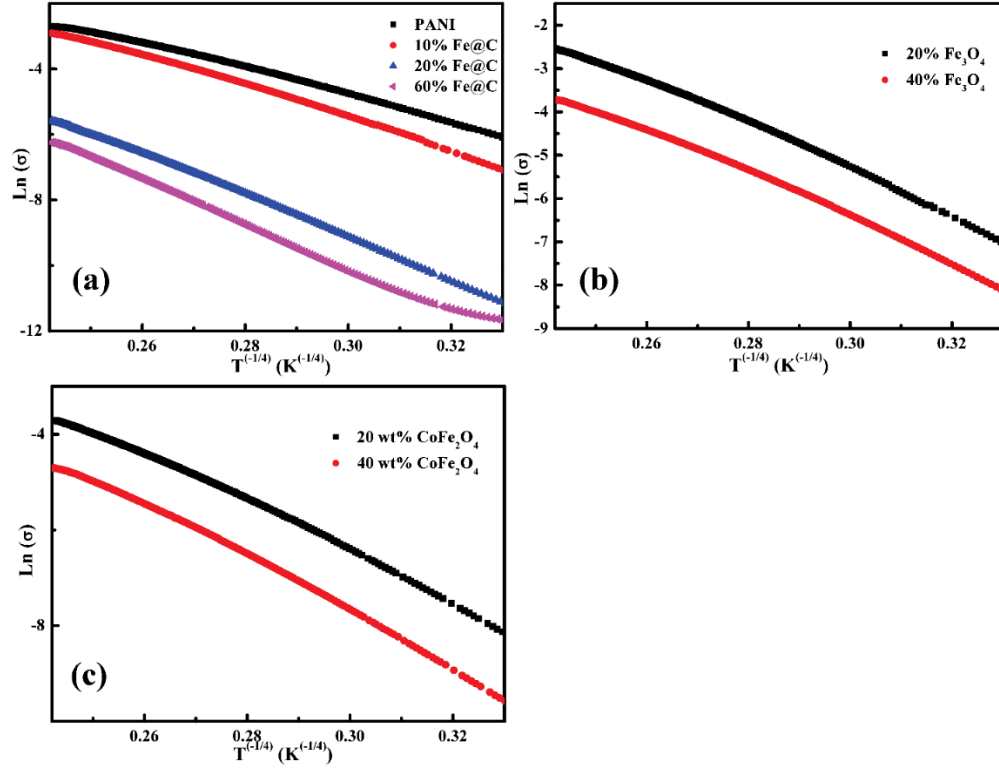


Figure 3.10 $\ln(\sigma)$ as a function of $T^{-1/4}$ of (a) Fe@C/PANI, (b) Fe_3O_4 /PANI and (c) CoFe_2O_4 /PANI nanocomposites.

In order to understand the charge transport in pure PANI and the magnetic PANI nanocomposites, the Mott variable range hopping (VRH) model was applied to study the electron transport mechanism,²⁵ and represented as equation 1:

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/(1+n)} \right] \quad n=1, 2, 3 \quad (1)$$

Where the n value of 3, 2, and 1 is for three-, two-, and one- dimensional systems, respectively.²⁶ The pre-exponential factor σ_0 is constant which represents the conductivity at infinite low temperature limit. T is the temperature in Kelvin (K), and T_0 is the characteristic Mott Temperature (K) and expressed as equation 2:²⁷

$$T_0 = 24 / [\pi k_B N(E_F) a_0^3] \quad (2)$$

Where a_0 is the localization length of the localized wave function of charge carriers, k_B is Boltzmann constant, and the $N(E_F)$ is the density of states at the fermi level.²⁶ The T_0 is related to the density of states at the fermi level and the localization length. The equation 1 can be rearranged to equation 3:

$$\ln \sigma = \ln \sigma_0 - \left(\frac{T_0}{T} \right)^{1/(1+n)} \quad n=1, 2, 3 \quad (3)$$

So, σ_0 and T_0 can be obtained from the intercept and slope of the plot of $\ln(\sigma) \sim T^{-1/(1+n)}$, respectively. The plot of $\ln(\sigma) \sim T^{-1/(1+n)}$ is shown in Figure 10. The pure PANI and the magnetic PANI nanocomposites are observed to follow a $\ln(\sigma) \sim T^{-1/4}$ linear relationship, which indicates a quasi 3-d VRH electrical conduction mechanism. The calculated σ_0 and T_0 values are summarized in Table 1. The obtained σ_0 and T_0 of pure PANI are lower than those of the magnetic PANI nanocomposites. For the Fe@C/PANI and CoFe₂O₄/PANI

Table 3.1 ρ_r , σ_0 and T_0 for the pure PANI, and magnetic PANI nanocomposites with different magnetic nanofillers.

Sample	ρ_r	σ_0 (S cm ⁻¹)	$T_0 \times 10^5$ (K)
Pure PANI	4.31	1705.1	28.00
10 wt%			
Fe@C/PANI	6.19	19447.0	70.60
20 wt%			
Fe@C/PANI	13.22	22434.6	166.07
60 wt%			
Fe@C/PANI	18.52	15971.6	185.88
20 wt% Fe ₃ O ₄ /PANI	6.94	59655.4	89.81
40 wt% Fe ₃ O ₄ /PANI	6.68	9122.5	75.25
20 wt%			
CoFe ₂ O ₄ /PANI	6.88	17777.7	88.36
40 wt%			
CoFe ₂ O ₄ /PANI	8.20	20547.4	122.41

nanocomposites, the T_0 increase with increasing the nanoparticle loading, however, $\text{Fe}_3\text{O}_4/\text{PANI}$ nanocomposites, T_0 decreases with increasing the nanoparticle loading. Generally, the T_0 is strongly dependent on the disorder (in PANI, the disorder means the sequence of quinoid–benzenoid groups is random) presented in the samples. And the resistivity ratio (ρ_r , $\rho_r = \rho_{150} / \rho_{290}$) can be used to measure the disorder.^{28, 29} The calculated resistivity ratio is summarized in **Table 3.1**. The T_0 display the same trend as ρ_r . It is obvious that the nanoparticle loading affects the ρ_r indicating that the appearance of nanoparticle could adjust the defects in the polymer matrix.³⁰ The calculated σ_0 did not show the same change trend as the disorder in the magnetic PANI nanocomposites.

3.3.7 MR

The MR can be calculated by using equation 4:

$$\text{MR}\% = \frac{R(H) - R(0)}{R(0)} \times 100 \quad (4)$$

where $R(0)$ is the resistance without magnetic field, and $R(H)$ is the resistance under the magnetic field H . **Figure 3.11** shows the MR value of pure PANI and the PANI nanocomposites with different magnetic nanoparticles at 290 K. For pure PANI and $\text{Fe@C}/\text{PANI}$ nanocomposites, **Figure 3.11(a)**, the MR of pure PANI is higher than those of $\text{Fe@C}/\text{PANI}$ nanocomposites with different Fe@C loading within the measured magnetic field range. The highest MR value of pure PANI is 22.5% at 5 T. The 10 wt% $\text{Fe@C}/\text{PANI}$ nanocomposites show lower MR value compared with $\text{Fe@C}/\text{PANI}$ nanocomposites with higher Fe@C loading. And then MR value of $\text{Fe@C}/\text{PANI}$ nanocomposites decrease with increasing the Fe@C loading. For both $\text{Fe}_3\text{O}_4/\text{PANI}$ and $\text{CoFe}_2\text{O}_4/\text{PANI}$ nanocomposites, **Figure 3.11(b&c)**, the MR increase with increasing the

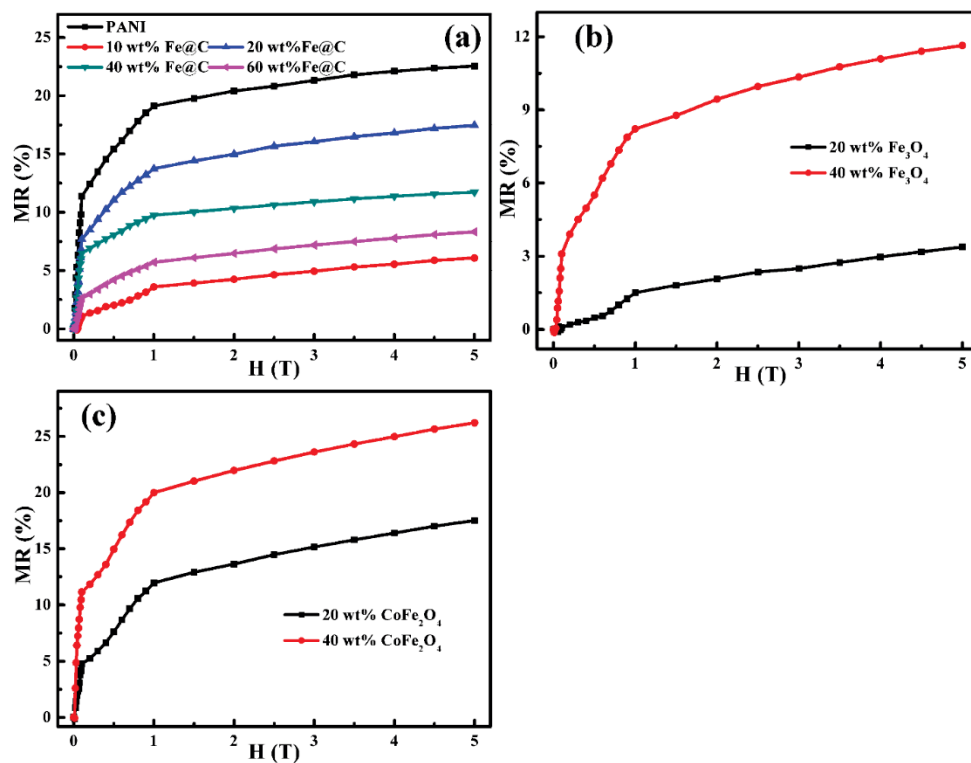


Figure 3.11 magnetoresistance of (a) pure PANI and Fe@C/PANI, (b) Fe₃O₄/PANI, and (c) CoFe₂O₄/PANI nanocomposites at 290 K.

nanoparticle loading. When the nanoparticle loading is 40 wt%, the CoFe₂O₄/PANI nanocomposites shows higher MR value (26.2% at 5T) than Fe@C/PANI (11.7 at 5T) and Fe₃O₄/PANI (11.6 at 5T). The slope of the materials at low magnetic field (around 0.1 T) reflects the sensitivity of the materials to the magnetic field.³¹ Following is the relationship of the slopes for the pure PANI and the PANI nanocomposites with different magnetic nanoparticles: 40 wt% CoFe₂O₄/PANI > pure PANI > 20 wt% Fe@C/PANI > 40 wt% Fe@C/PANI > 20 wt% CoFe₂O₄/PANI > 40 wt% Fe₃O₄/PANI > 60 wt% Fe@C/PANI > 10 wt% Fe@C/PANI > 20 wt% Fe₃O₄/PANI. Therefore, the 40 wt% CoFe₂O₄/PANI nanocomposites with higher sensitivity to the external magnetic field have the potential to be used as magnetic field sensor.³²

Generally, the wave-function shrinkage model can be used to describe the positive MR of highly disorderedly localized systems in the VRH regime.³³ In the temperature dependent resistivity section, the pure PANI and magnetic PANI nanocomposites exhibit quasi 3-*d* Mott VRH electrical conduction mechanism. Therefore, the wave-function shrinkage model can be applied to the pure PANI and magnetic PANI nanocomposites. In the wave-function shrinkage model, the $R(H,T)/R(0,T)$ can be expressed as equation 5:³⁴

$$R(H,T)/R(0,T) = \exp\{\xi_c(0)[\xi_c(H)/\xi_c(0) - 1]\} \quad (5)$$

where $\xi_c(0) = (T_0/T)^{1/4}$ for the 3-*d* Mott VRH charge transport mechanism, $\xi_c(H)/\xi_c(0)$ is the normalized hopping probability parameter and is a function of H/P_C for the Mott VRH charge transport mechanism, H is the magnetic field, P_C is the fitting parameter, which is the normalizing characteristic field that must be extracted from one set of MR

ratio data points and can also be given by equation 6 for the Mott VRH charge transport mechanism.^{30, 34, 35}

$$P_C = 6\hbar / [ea_0^2 (T_0 / T)^{1/4}] \quad (6)$$

where $\hbar$ is the reduced Planck's constant, e is electron charge. In the low magnetic field, the equation 5 is simplified to equation 7:³³

$$R(H, T) / R(0, T) \approx 1 + t_2 \frac{H^2}{P_C^2} \left(\frac{T_0}{T} \right)^{1/4} \quad (7)$$

The MR can be expressed as equation 8:

$$\text{MR} = \frac{R(H, T) - R(0, T)}{R(0, T)} \approx t_2 \frac{H^2}{P_C^2} \left(\frac{T_0}{T} \right)^{1/4} = t_2 \frac{e^2 a_0^4}{36\hbar^2} \left(\frac{T_0}{T} \right)^{3/4} H^2 \quad (8)$$

where t_2 is 5/2016. According to equation 8, the MR value is always positive in the wave-function shrinkage model, which can be applied to explain the positive MR values of the PANI nanocomposites with different magnetic nanoparticles. The localization length a_0 can be obtained from the slope of the curve by plotting $MR \sim H^2$. The a_0 can also be calculated from equation 9:

$$a_0^4 = \frac{36\hbar^2 MR}{t_2 e^2} \left(\frac{T_0}{T} \right)^{-3/4} H^{-2} \quad (9)$$

The calculated a_0 decreases with increasing the H. The density of state at the fermi level $N(E_F)$ can be calculated from equation 10:

$$N(E_F) = 24 / [\pi k_B T_0 a_0^3] \quad (10)$$

The obtained $N(E_F)$ is summarized in **Table 3.2**. Generally, the hopping probability between the localized states increase with increasing the $N(E_F)$, indicating that the higher

Table 3.2 a_0 , $N(E_F)$ and R_{hop} for the pure PANI, and magnetic PANI nanocomposites with different magnetic nanofillers.

Sample	Parameters	Magnetic Field (T)		
		1.0	2.0	5.0
Pure PANI	a_0 (nm)	33.34	23.96	15.53
	$N(E_F)$ ((J cm ³) ⁻¹)	5.33×10^{33}	1.44×10^{34}	5.27×10^{34}
	R_{hop} (nm)	123.94	89.07	57.74
20 wt%	a_0 (nm)	14.19	10.86	7.77
Fe ₃ O ₄ /PANI	$N(E_F)$ ((J cm ³) ⁻¹)	2.15×10^{34}	4.81×10^{34}	1.31×10^{35}
	R_{hop} (nm)	70.61	54.04	38.65
20 wt%	a_0 (nm)	23.90	17.46	12.30
CoFe ₂ O ₄ /PANI	$N(E_F)$ ((J cm ³) ⁻¹)	4.57×10^{33}	1.18×10^{34}	3.36×10^{34}
	R_{hop} (nm)	118.42	86.52	60.95
20 wt%	a_0 (nm)	21.98	15.88	10.43
Fe@C/PANI	$N(E_F)$ ((J cm ³) ⁻¹)	3.14×10^{33}	8.31×10^{33}	2.93×10^{34}
	R_{hop} (nm)	127.53	92.14	60.54
60 wt%	a_0 (nm)	17.27	12.61	8.49
Fe@C/PANI	$N(E_F)$ ((J cm ³) ⁻¹)	5.76×10^{33}	1.49×10^{34}	4.86×10^{34}
	R_{hop} (nm)	103.15	75.22	50.66

$N(E_F)$, the more hopping probability of charge carriers. The average hopping length R_{hop} can be obtained from equation 11:³⁶

$$R_{\text{hop}} = (3/8)(T_0/T)^{1/4} a_0 \quad (11)$$

The obtained R_{hop} is summarized in **Table 3.2**. For the pure PANI and PANI nanocomposites with different magnetic nanoparticles, the a_0 and R_{hop} decrease with increasing H , the $N(E_F)$ increases with increasing the magnetic field. For the Fe@C/PANI nanocomposites, the a_0 and R_{hop} decrease with increasing the Fe@C loading; the $N(E_F)$ increases with increasing the Fe@C loading. For the PANI nanocomposites with different magnetic nanoparticles at the same loading level, the MR, a_0 , R_{hop} and $N(E_F)$ are affected by the type of the magnetic nanoparticles.

3.3.8 Magnetic property

Magnetization (M) is a phenomenon which describes the response of the magnetic materials to an external magnetic field. The direction of the magnetic moment of magnetic materials are the same as the applied magnetic field direction, and the magnetization increases with increasing the magnetic field until it reaches the saturation magnetization (M_s).¹⁴ **Figure 3.12** shows the magnetization curves of the as-received magnetic nanoparticles and the magnetic PANI nanocomposites at room temperature. The hysteresis loops are observed in all the samples. For pure Fe@C nanoparticles, **Figure 3.12(a)**, the coercivity (H_c) is 116.4 Oe. Compared with pure Fe@C nanoparticles, the H_c of Fe@C/PANI nanocomposites (156.6 Oe for 20 wt% Fe@C/PANI nanocomposites; 713.4 Oe for 40 wt% Fe@C/PANI nanocomposites) are higher. The Fe₃O₄/PANI and CoFe₂O₄/PANI nanocomposites, **Figure 3.12(b&c)**, also show higher H_c than those of pure

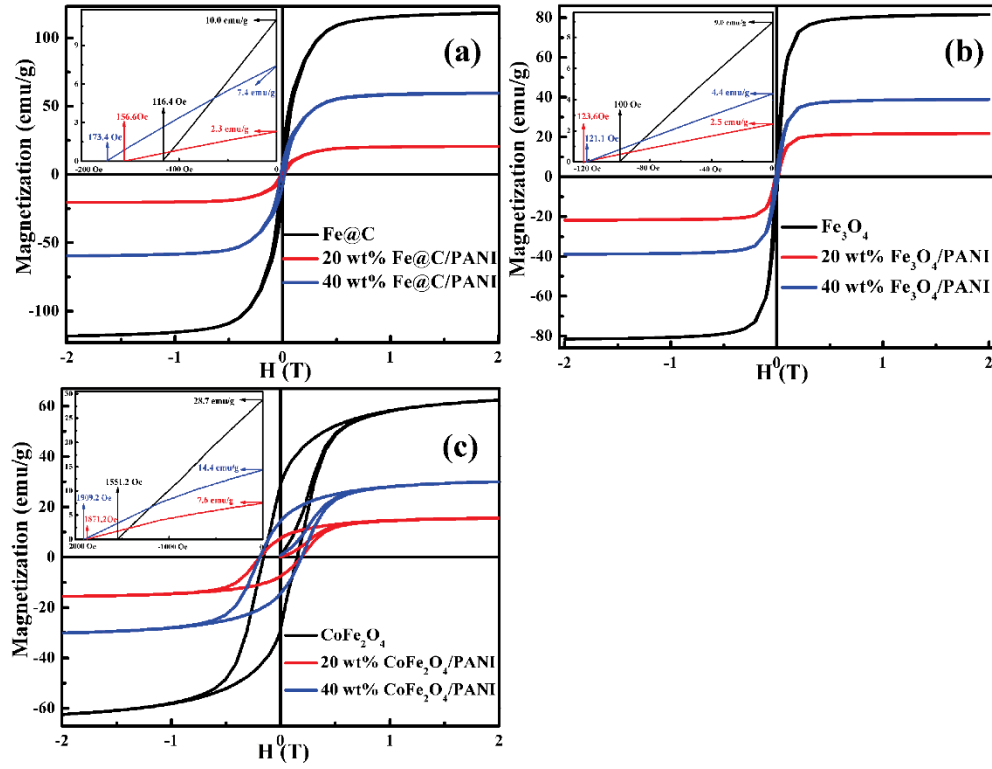


Figure 3.12 Room temperature magnetization as a function of magnetic field for (a) Fe@C/PANI, (b) Fe₃O₄/PANI, and (c) CoFe₂O₄/PANI nanocomposites.

nanoparticles. It is observed that the M of all the samples did not reach saturation within the measured magnetic field. The saturation magnetization could be determined by the extrapolated M_s obtained from the intercept of $M \sim H^{-1}$ at high magnetic field.¹⁹ The obtained M_s of Fe@C, Fe₃O₄ and CoFe₂O₄ is 120.89, 82.75 and 67.05 emu/g, respectively. The M_s is 61.10, 39.40 and 32.16 emu/g for 40 wt% Fe@C/PANI, 40 wt%Fe₃O₄/PANI, and 40 wt% CoFe₂O₄/PANI nanocomposites respectively. According to the calculated M_s , the weight percent of the nanoparticle in the magnetic PANI nanocomposites could be calculated. The calculated weight percent of nanoparticle in the 40 wt% Fe@C/PANI, 40 wt% Fe₃O₄/PANI, and 40 wt% CoFe₂O₄/PANI is 50.5, 47.6 and 48.0%, respectively, which is consistent with the initial weight percent of nanoparticles in PANI nanocomposites.

3.4 Conclusion

The conductive PANI nanocomposites with different magnetic nanoparticles have been successfully synthesized using the SIP method. The results from SEM and TEM show that the magnetic nanoparticles have been embedded in the PANI matrix. The resistivity of the magnetic PANI nanocomposites decreases with increasing temperature, exhibiting semiconducting behavior. Mott VRH model is introduced to evaluate the electrical conduction mechanism of the PANI and magnetic PANI nanocomposites, and the results indicate a quasi 3- d VRH mechanism. The positive MR is observed in the PANI nanocomposites, and the type of magnetic nanoparticles affects the MR behavior of the PANI nanocomposites. The wave-function shrinkage model is applied to study the response of the localization length, density of state at fermi level and average hoping length

to the applied magnetic field. The enhanced dielectric property is observed in the magnetic PANI nanocomposites.

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Chapter 4. Enhanced Negative Magnetoresistance and Magnetic Field

Sensitivity of Polyaniline Interfaced with Nanotitania

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Abstract

Unique negative giant magnetoresistance (GMR) of up to -43 % at room temperature was observed in the 10 wt% titania/polyaniline (TiO₂/PANI) nanocomposites prepared by simple oxidation polymerization. And the negative MR value was further evaluated using forward interference model. Other properties were tested and comparatively reported. The resistivity of TiO₂/PANI nanocomposites decreased with increasing temperature, indicating a semiconductor behavior. The Mott variable range hopping (VRH) approach indicated that TiO₂/PANI nanocomposites are disordered systems in the 3-dimensional VRH regime. The scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) were also used to study morphology, chemical and crystal structure of the nanocomposites. The thermogravimetric analysis (TGA) was used to study the thermal stability of the TiO₂/PANI nanocomposites.

4.1 Introduction

Intrinsic magnetoresistance (MR) reflects the resistance change of a material as a function of an external magnetic field.^{1, 2} The MR effect has been found in conductive polymer nanocomposites reinforced with different nanoparticles, such as the ultrahigh MR sensitivity observed in tungsten trioxide/polyaniline (PANI) nanocomposites when exposed to a low magnetic field.³ and the positive and negative MR effect found in magnetic electrospun fibers of polyacrylonitrile-based carbon nanocomposites.⁴ In the past decade, conductive polymer nanocomposites have attracted intensive research interest for their potential applications as pseudocapacitors, electrode materials, electronic devices, magnetic field sensors, electrocatalysts, microwave absorbers, energy electrodes, and biosensors,⁵⁻⁷ owing to their low cost, light weight, flexibility, high capacitance, electrical conductivity, unique optical and magnetic properties.^{5, 6, 8-10} Among reported conductive polymers, PANI has been viewed as one of the most promising conjugated polymers^{11, 12} due mainly to its high conductivity, good environmental stability, high pseudocapacitive properties, and controllable doping levels.^{11, 13, 14} PANI has been well-studied for various promising potential applications, including supercapacitor materials, environment remediation agents (eg. reduction of toxic Cr^{6+} in waste water), coupling agent between epoxies and nanofillers, anticorrosion coatings, gas sensors, solar cells, electromagnetic shielding materials, electrochromic devices, and among others.^{10, 15-22} Recently, our group has also reported nanocomposites composed of multi-wall carbon nanotube coated with PANI for electrochemical energy storage²³ and magnetic PANI nanocomposites for toxic hexavalent chromium removal²⁴ further demonstrating the potential broad-spectrum

application of PANI-based materials. Even though, previous studies on TiO₂ have shown its promise as functional nanostructures in solar cells, catalysis, dielectric ceramics, optoelectronic devices, air filters, and self-cleaning agents, there are only a few reports on TiO₂/PANI nanocomposites.²⁵⁻²⁷ Among these previous studies, Zhang *et al* reported a template-free preparation of TiO₂/PANI microspheres and studied the effect of TiO₂ content on the conductivity, morphology, and hydrophilicity of the as-prepared TiO₂/PANI materials.^{28, 29} Dey *et al* reported the dielectric properties of TiO₂/PANI nanocomposites and studied the effect of TiO₂/PANI interface on the materials' dielectric properties.²⁷ Li *et al* reported gas sensing application of TiO₂/PANI nanocomposites.³⁰ However, the MR effect of TiO₂/PANI nanocomposites has not been reported until now.

In this study, titanium dioxide (TiO₂)/PANI nanocomposites were prepared by dispersing TiO₂ nanoparticles within in-situ synthesized PANI matrix through a surface initiated polymerization (SIP) method. The SIP method was utilized to disperse TiO₂ nanoparticles within hosting PANI matrix. Scanning electron microscopy (SEM) was employed to characterize the morphology of the as-received TiO₂ nanoparticles, pure PANI, and the as-prepared TiO₂/PANI nanocomposites. High resolution transmission electron microscopy (HRTEM) was utilized to confirm the dispersion of TiO₂ nanoparticles in the polymer matrix. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) studies were performed to characterize the nanocomposites' chemical structures and crystalline structures, respectively. The thermal stability of TiO₂/PANI nanocomposites was further characterized using thermogravimetric analysis (TGA). More importantly, the optical properties, frequency dependent permittivity at room temperature,

temperature dependent resistivity, electron transport mechanism, and MR were thoroughly characterized and analyzed in this study. A negative MR was observed in the synthesized TiO₂/PANI nanocomposite samples at room temperature, and was further evaluated on the basis of orbital magnetoconductivity theory.

4.2 Experimental

4.2.1 Materials

Aniline (C₆H₇N), ammonium persulfate (APS, (NH₄)₂S₂O₈, 98%) and *p*-toluene sulfonic acid (PTSA, C₇H₈O₃S, ≥ 98.5%) were purchased from Sigma-Aldrich. The TiO₂ nanoparticles were obtained from Nanostructured & Amorphous Materials, Inc. All the chemicals were used as-received without any further treatment.

4.2.2 Fabrication of TiO₂/PANI nanocomposites

TiO₂/PANI nanocomposites were fabricated using the SIP method. Firstly, the TiO₂ nanoparticles were dispersed in an aqueous solution containing PTSA (15 mmol) and APS (9 mmol) in 100 mL deionized water by one-hour sonication and mechanical stirring in an ice-water bath. Secondly, the aniline solution (18 mmol, 25 mL deionized water) was mixed with the above TiO₂ nanoparticles suspension and mechanically and ultrasonically stirred continuously for additional 1.5 hours in the ice-water bath for further polymerization. The product was vacuum filtered and washed with deionized water several times to remove any unreacted PTSA and APS. The final synthesized nanocomposites were dried at 50 °C in an oven overnight. The TiO₂/PANI nanocomposites with a nanoparticle loading of 2.0, 5.0, 8.0, and 10.0 wt% were fabricated, respectively. Pure PANI was

fabricated following the above procedures without adding any nanoparticles for comparison.

4.2.3 Characterizations

The morphologies of the synthesized samples were examined by a Hitachi S4300 SEM. All the samples were sputter coated a thin layer of gold (about 5 nm) to ensure good conductivity. The HRTEM was performed on the Hitachi H9000NAR. The FT-IR spectra of the products were obtained on a Nicolet IS 10 (in the range of 650 to 4000 cm^{-1} at a resolution of 4 cm^{-1}). XRD was measured by D/max-rB wide-angle X-ray diffractometer at a $\text{Cu } k_{\alpha}$ wavelength of 0.154 nm. TGA analysis was conducted by TA instruments TGA Q-500 with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under an air-flow rate of 60 mL min^{-1} from 25 to 800 $^{\circ}\text{C}$. The scanning rate is 4 $^{\circ} \text{min}^{-1}$ from 10 to 80 $^{\circ}$. UV-vis spectra of pure PANI and its TiO_2 nanocomposites were obtained on a UV/VIS/NIR spectrophotometer (PC, JASCO Model V-670). Dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of 20 to 2×10^6 Hz at room temperature. As-received TiO_2 , pure PANI and TiO_2/PANI nanocomposites were pressed in a form of disc pellet with a diameter of 25 mm by a hydraulic presser. The same samples were also used to measure the resistivity and MR. The temperature dependent resistivity was measured by a standard four-probe method from 50 to 290 K. MR was carried out using a standard four-probe technique by a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design at 130 and 290 K, respectively. The configuration of MR measurements are perpendicular (B perpendicular to sample surface).

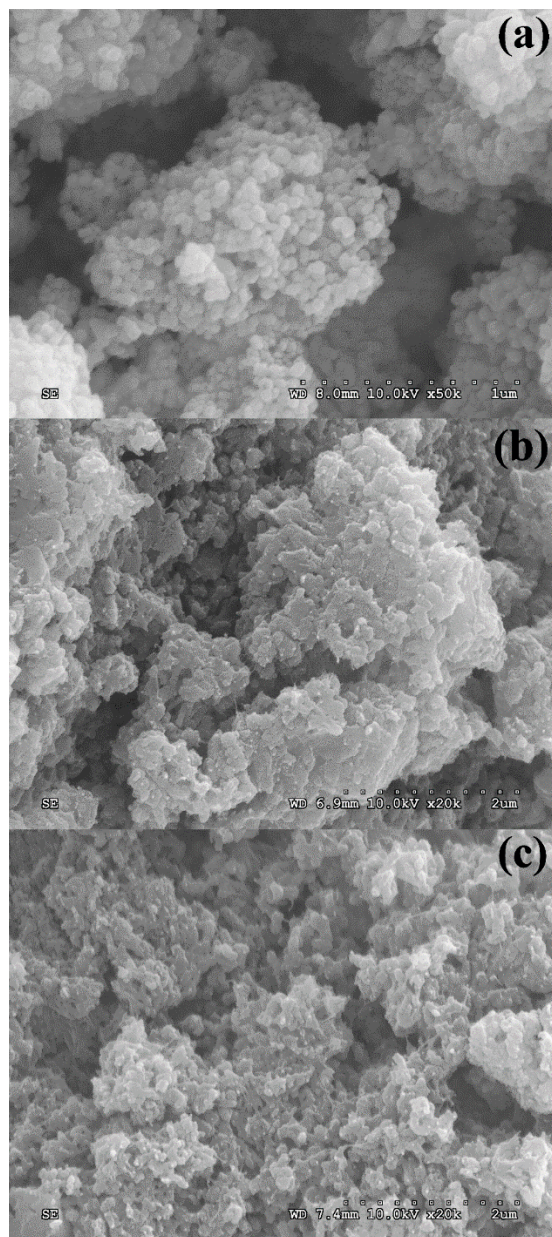


Figure 4.1 SEM images of (a) as-received TiO_2 nanoparticles, (b) pure PANI and (c) TiO_2 /PANI with 5.0 wt% TiO_2 .

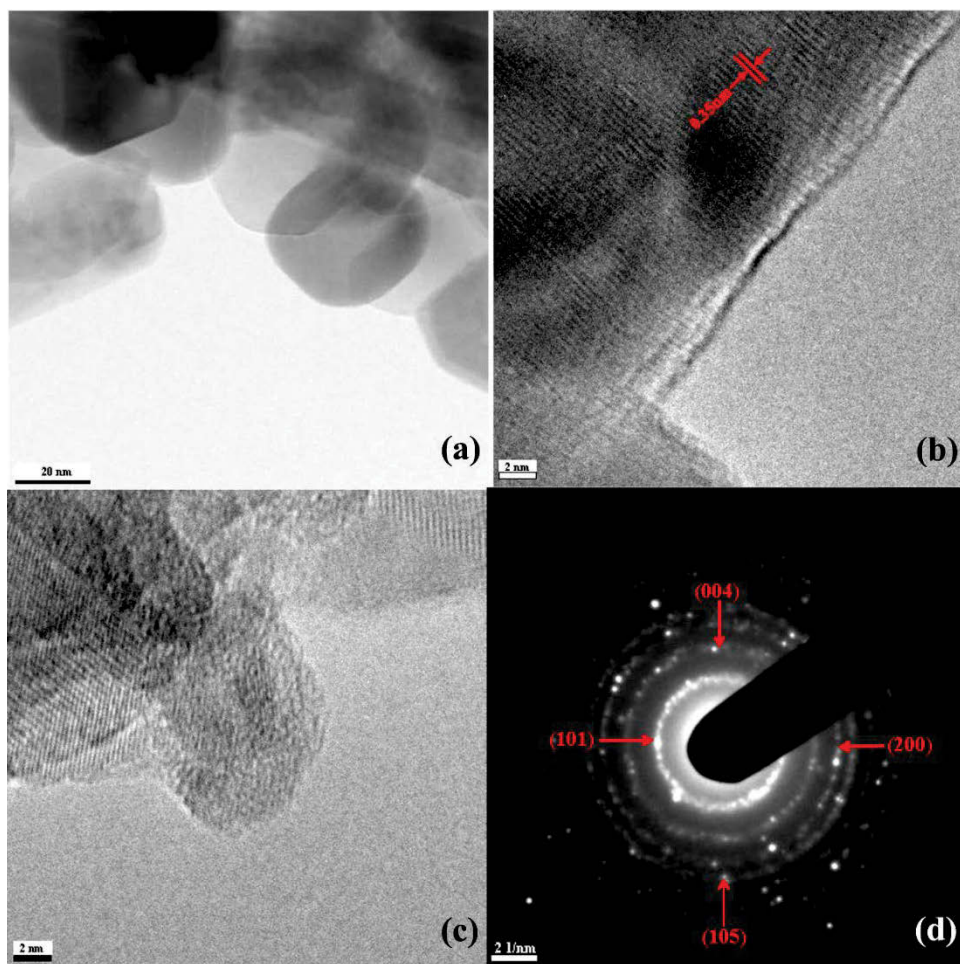


Figure 4.2 HRTEM images of (a, b) as-received TiO_2 nanoparticles, (c) PANI nanocomposites with 10.0 wt% TiO_2 , and selected area electron diffraction (SAED) of TiO_2 /PANI nanocomposites with 10.0 wt% TiO_2 .

4.3 Results and discussions

4.3.1 Microstructure of the nanocomposites

The SEM images in **Figure 4.1** show the morphological features of the as-received TiO₂ nanoparticles, pure PANI, and the TiO₂/PANI nanocomposites reinforced with 5.0 wt% TiO₂ nanoparticles. As seen in **Figure 4.1a**, the as-received TiO₂ nanoparticles exhibit a spherical morphology with an average 50 nm diameter as measured by a Nano measure software and the surface of these TiO₂ nanoparticles is fairly smooth. In contrast, rough and flake-like topographical features were seen in pure PANI, **Figure 4.1b**. The TiO₂/PANI nanocomposites containing 5.0 wt% TiO₂ nanoparticles exhibit rough and flake-like morphology, showing similarity to that of pure PANI polymer powders suggesting the dispersion of TiO₂ nanoparticles in PANI matrix. The above observation is also in agreement with a previous report on TiO₂/PANI nanocomposites.³¹ **Figure 4.2(a&b)** show the TEM images of the as-received TiO₂ nanoparticles. The lattice fringes of the TiO₂ nanoparticles were clearly observed in **Figure 4.2b**. The lattice fringe *d*-spacing of about 0.35 nm, as measured by the Nano measure software corresponds to the (101) crystallographic plane of TiO₂.³² **Figure 4.2c** shows the microstructure of the TiO₂/PANI nanocomposites with 10.0 wt% TiO₂, which consist of TiO₂ inside and amorphous PANI layer outside. The lattice fringes of TiO₂ were also observed. The selected area electron diffraction (SEAD, **Figure 4.2d**) was used to identify the crystal structure of TiO₂/PANI nanocomposites with 10.0 wt% TiO₂. The calculated *d*-spacing values of 0.351, 0.238, 0.1873 and 0.169 nm correspond to (101), (004), (200) and (105) crystallographic planes of TiO₂.^{33, 34}

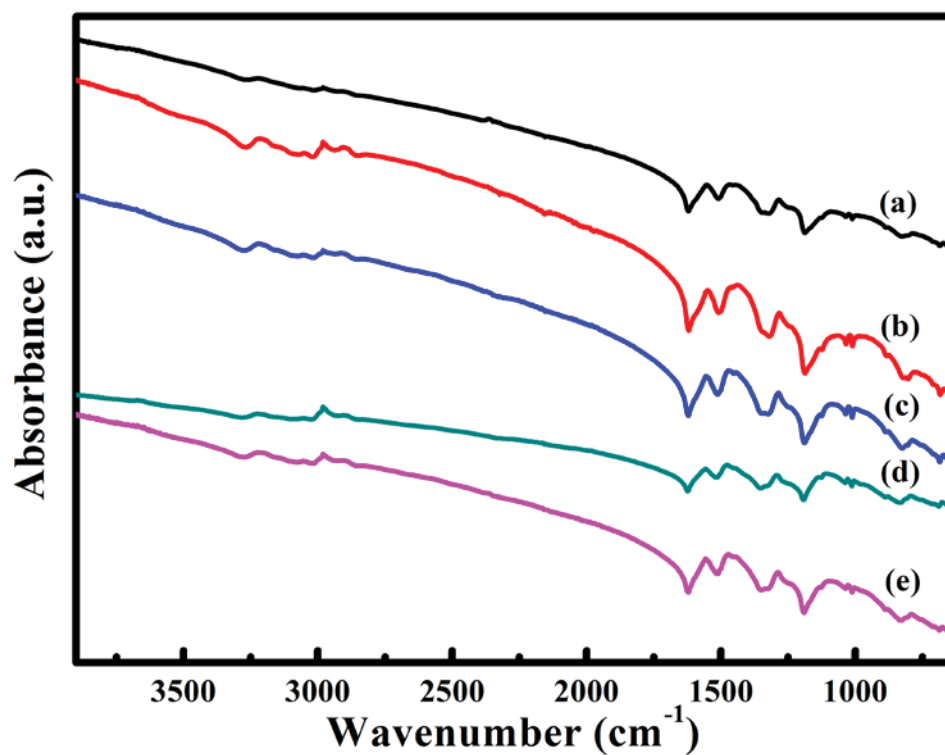


Figure 4.3 FT-IR spectra of (a) pure PANI and TiO₂/PANI nanocomposites with a TiO₂ loading of (b) 2.0, (c) 5.0, (d) 8.0 and (e) 10.0 wt%.

4.3.2 FT-IR analysis

Figure 4.3 shows the FT-IR spectra of pure PANI and its TiO₂ nanocomposites loaded with different amount of TiO₂ nanoparticles. The peak at 3221 cm⁻¹ is correlated to the N-H stretching,⁵ while the C=C stretching vibration of the quinoid and benzenoid rings in pure PANI appear at around 1555 and 1466 cm⁻¹,³⁵ respectively, **Figure 4.3a**. The 1283 cm⁻¹ peak can be assigned to the C-N stretching vibration of benzenoid units.^{5,36} Two peaks at 1237 and 785 cm⁻¹ are related to the C-H in-plane vibration of the quinoid rings and the out-of-plane bending of C-H in the substituted benzenoid rings, respectively.⁹ The FT-IR spectra for pure PANI are consistent with previous spectroscopic characterization.⁵ The characteristic peaks of pure PANI were also observed in the TiO₂/PANI nanocomposite, **Figure 4.3(b, c, d & e)**. However, compared with those peaks observed in pure PANI, the same peaks have a slight shift (about 1~9 cm⁻¹) due mainly to the interactions between TiO₂ and PANI, which result in the electrical charge delocalization on the polymer backbone at the interface.⁵

4.3.3 X-ray diffraction analysis

Figure 4.4 shows the XRD patterns of the TiO₂ nanoparticles, pure PANI and its TiO₂ nanocomposites loaded with different amount of TiO₂ nanoparticles. The diffraction peaks located at 25.4, 37.83, 48.07, 54.20, 55.33, 62.91, 68.96, 70.4 and 75.17° are indexed to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) anatase phase of the TiO₂ nanoparticles³⁷ and the diffraction peak located at 2θ = 27.50 corresponds to the (110) rutile phase of the TiO₂,^{33, 38} **Figure 4.4a**. For pure PANI, the two broad diffraction peaks located at 2θ = 20.08 and 25.33° (see **Figure 4.4b**), corresponds to the

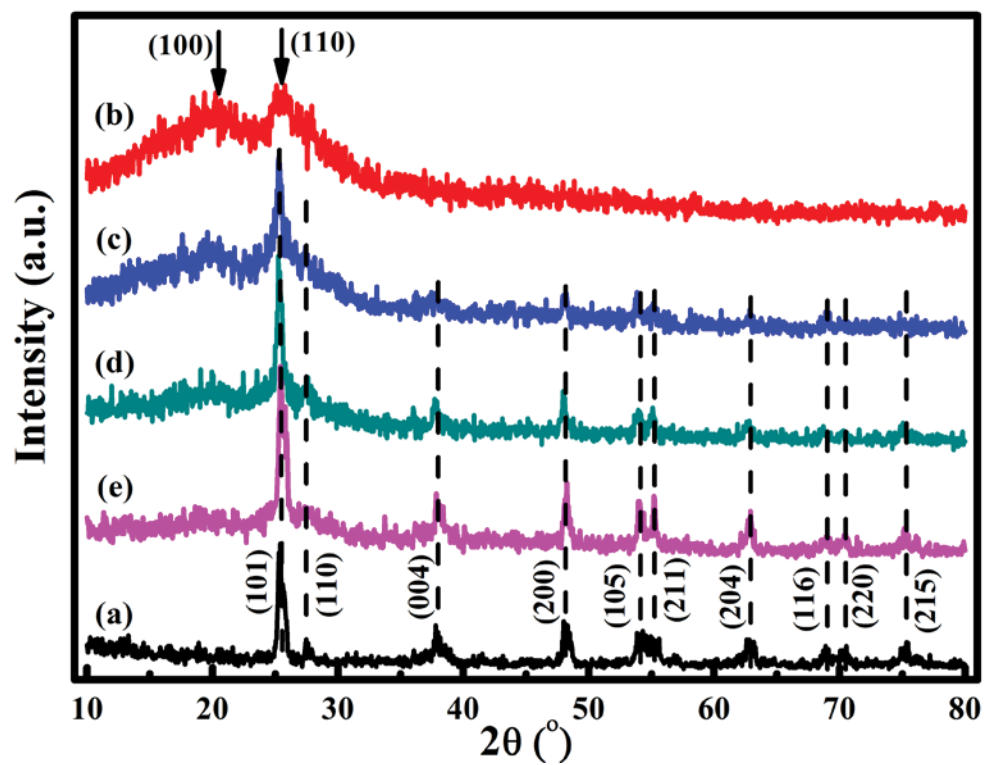


Figure 4.4 The XRD patterns of (a) as-received TiO_2 nanoparticles, (b) pure PANI and TiO_2/PANI nanocomposites with a TiO_2 loading of (c) 2.0, (d) 5.0 and (e) 10.0 wt %.

(100) and (110) crystallographic planes of the partially crystalline PANI.¹³ The crystallinity of PANI is about 18.2%, which was achieved from the XRD data. The diffraction peaks of TiO₂ and PANI were also observed in the TiO₂/PANI nanocomposites, **Figure 4.4(c, d&e)**. The intensity of the diffraction peaks of TiO₂ increases with increasing the TiO₂ nanoparticle loading, however, the intensity of the two original peaks of pure PANI decreases with increasing the TiO₂ nanoparticle loading. Above results suggest that the added TiO₂ nanoparticles exert an influence on the crystalline structure of the PANI matrix, implying the existence of an interaction between the PANI backbone and TiO₂ surface.

4.3.4 Thermogravimetric analysis

The TGA curves of TiO₂ nanoparticles, pure PANI, and its TiO₂ nanocomposites loaded with different amount of TiO₂ nanoparticles were shown in **Figure 4.5**. Almost no weight loss between 30 to 800 °C was observed for the as-received TiO₂ nanoparticles, indicating the high thermal stability of the as-received TiO₂ nanoparticles.³⁹ A weight residue about 0.93 wt% was observed for pure PANI, which could be due to the carbonization of pure PANI.⁹ Similar weight loss tendency was also observed in the TGA results of the TiO₂/PANI nanocomposites. The first weight loss stage between room temperature and 311 °C is attributed to the elimination of moisture and the decomposition of doped acid from PTSA in PANI.⁶ The second weight loss stage from about 311 to 649 °C is correlated to the thermal decomposition of the PANI chains.⁴⁰ The weight residues at 800 °C for the TiO₂/PANI nanocomposites loaded with 2.0, 5.0, 8.0, and 10.0 wt% TiO₂ nanoparticles are 4.3, 10.6, 14.9, and 17.8%, respectively. The weight residue is slightly

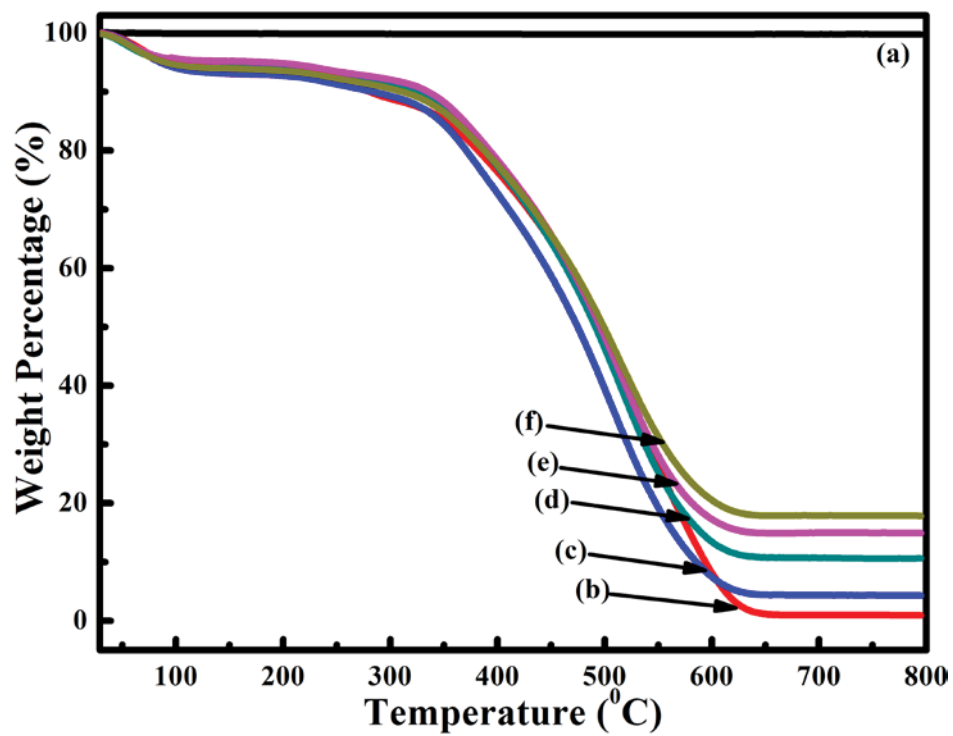


Figure 4.5 TGA curves of (a) as-received TiO₂ nanoparticles, (b) pure PANI and TiO₂/PANI nanocomposites with TiO₂ loading of (c) 2.0, (d) 5.0, (e) 8.0 and (f) 10.0 wt%.

higher than the initial calculated nanoparticle loadings, which could arise from the incomplete polymerization of aniline monomers during the SIP process.¹³

4.3.5 Dielectric properties

Dielectric properties reflect the polarization abilities of an electrical medium under an external electric field.^{13, 41} For polymer nanocomposites, both charge carrier motion within the hosting polymer matrix and the interfacial polarization between the matrix and the nanoparticles contribute to the observed dielectric properties.^{9, 42} The permittivity is represented as a complex permittivity, $\varepsilon^*(\omega)$, and is calculated as equation 1:¹³

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (1)$$

where $\omega = 2\pi f$ and f is the measuring frequency, the ε' and ε'' are the real and imaginary parts of ε^* , corresponding to the energy storage and dissipation within the medium, respectively, ε_s is the permittivity at low frequency limit, ε_∞ is the permittivity at high frequency limit, and τ is the relaxation time that is recorded when the materials return to the original state upon removing the applied electric field.

Figure 4.6 depicts the ε' , ε'' , and dielectric loss (i.e, $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$) as a function of frequency for pure PANI and the TiO₂/PANI nanocomposites loaded with 2.0, 5.0, 8.0 and 10.0 wt% TiO₂ nanoparticles at room temperature. The dielectric properties of the as-received TiO₂ nanoparticles are shown in **Figure 4.7**. Both pure PANI and TiO₂/PANI nanocomposites show the positive ε' , **Figure 4.6a**. The decreasing permittivity with increasing the frequency is attributed to the commonly known dielectric relaxation

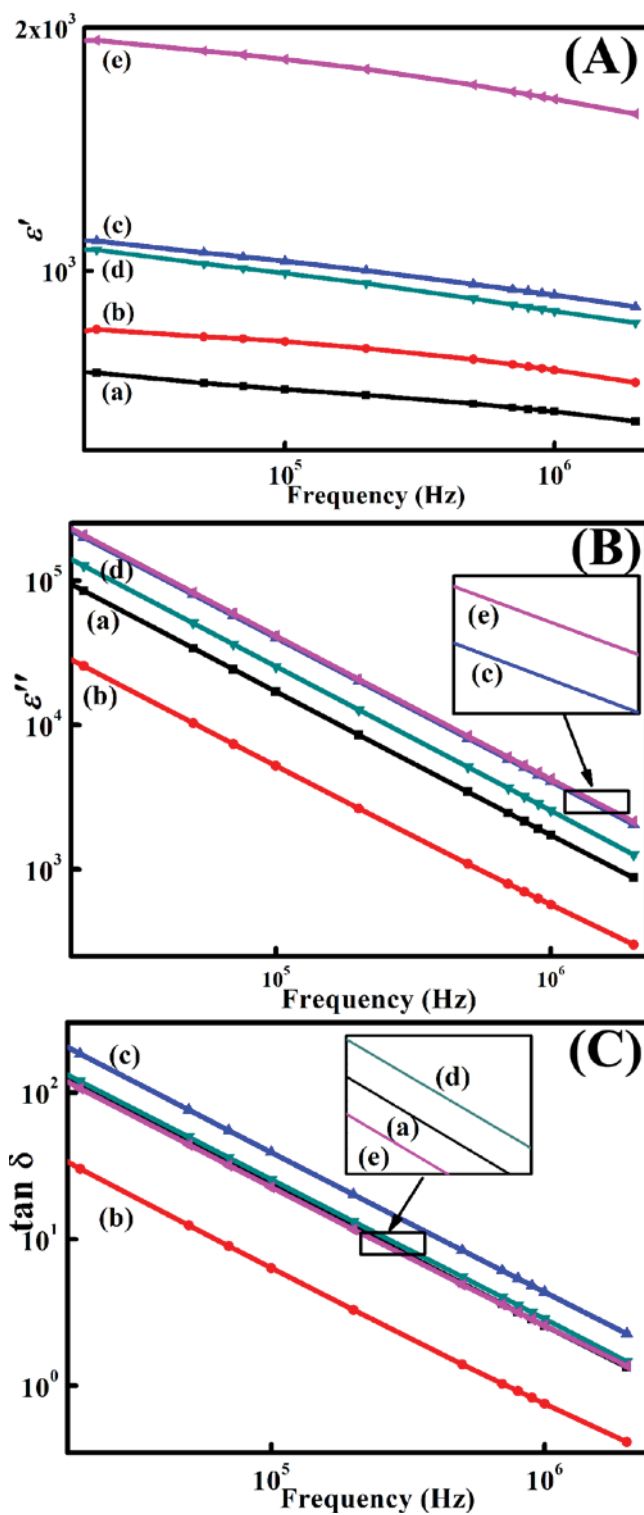


Figure 4.6 (A) Real permittivity, (B) imaginary permittivity, and (C) dielectric loss as a function of frequency of (a) pure PANI, TiO₂/PANI nanocomposites with a TiO₂ loading of (b) 2.0, (c) 5.0, (d) 8.0 and (e) 10.0 wt%.

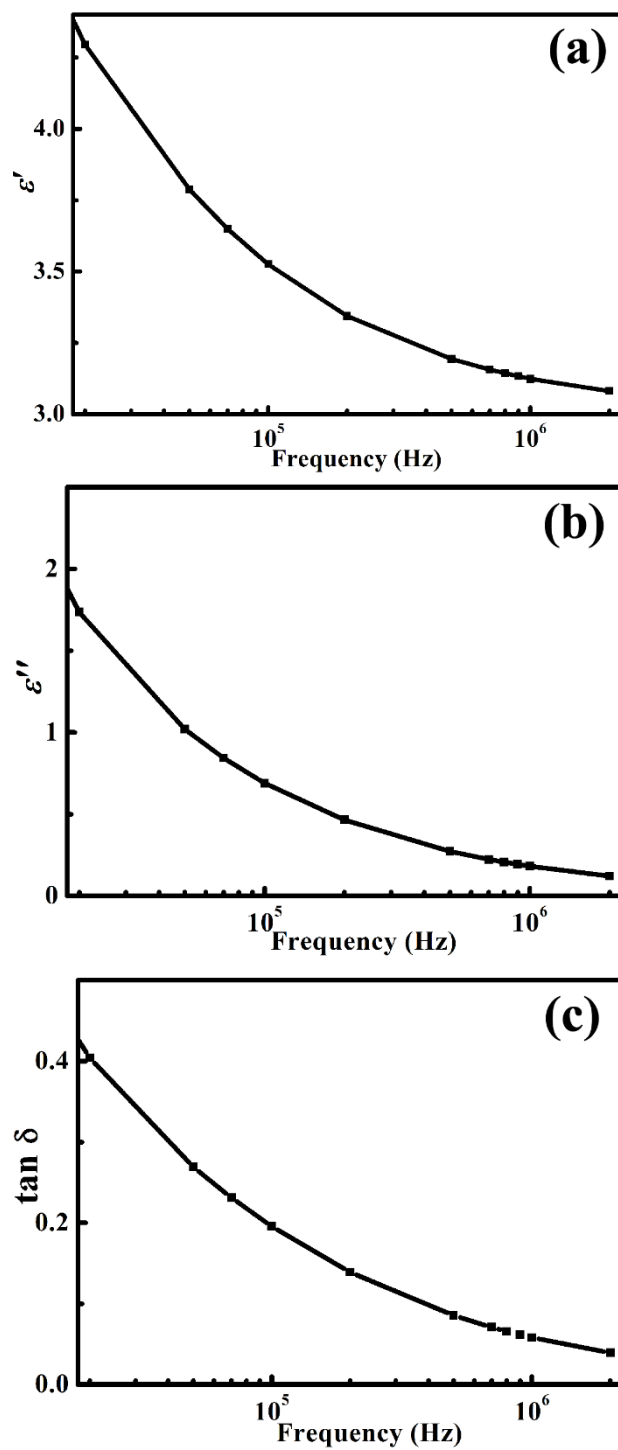


Figure 4.7 (a) Real permittivity, (b) imaginary permittivity, and (c) dielectric loss as a function of frequency of the as-received TiO_2 nanoparticles.

phenomena that reflects the delayed molecular polarization under an applied alternative electric field.^{1, 10} The TiO₂/PANI nanocomposites with different TiO₂ nanoparticle loadings show higher ε' values than that of pure PANI, attributing to interfacial polarization. Originating from the Maxwell-Wagner-Sillars polarization that usually occurs at the inner dielectric boundary layers on the mesoscopic scale. The interfacial polarization tends to occur when the charge carriers are accumulated at the interfaces between the hosting PANI and TiO₂ nanoparticles.^{5, 43} A higher positive ε' is observed at 2×10^4 Hz for the nanocomposites loaded with 10.0 wt% TiO₂ nanoparticles, indicating that the mobile charges are no longer free and localized in each metallic island.⁴⁴ For the as-received TiO₂ nanoparticles, **Figure 4.7a**, a decrease in ε' was observed when the frequency was increased. The ε' value of the as-received TiO₂ nanoparticles decreased from 4.3 to 3.1 within the measured frequency range. Compared with pure PANI and its TiO₂ nanocomposites, the ε' of the as-received TiO₂ nanoparticles is almost constant. **Figure 4.6b** shows the ε'' versus frequency for pure PANI and its TiO₂ nanocomposites. The ε'' decreases with increasing the frequency within the frequency scale, indicating that the dissipation of energy decreases with increasing the frequency. **Figure 4.6c** depicts the frequency dependent $\tan\delta$ for pure PANI and its TiO₂ nanocomposites with different TiO₂ nanoparticle loadings. The $\tan\delta$ of pure PANI and its nanocomposites shows a similar tendency as ε'' , The $\tan\delta$ of TiO₂/PANI nanocomposites decreases with increasing the frequency and the magnitude is ranging from 10^2 to 10^{-1} within the frequency range from 2×10^4 to 2×10^6 Hz.

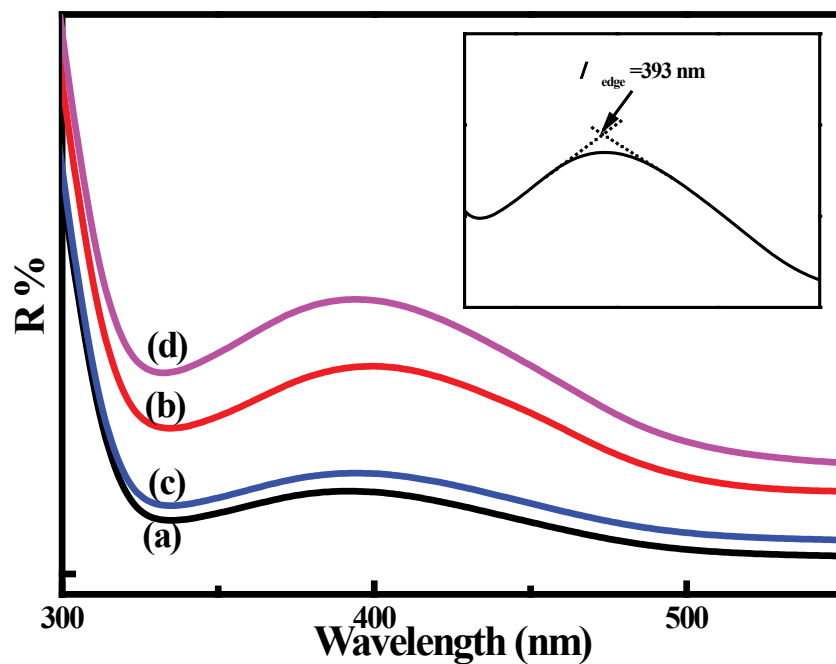


Figure 4.8 UV-vis DRS of (a) pure PANI and TiO_2/PANI nanocomposites with a TiO_2 nanoparticle loading of (b) 2.0, (c) 5.0 and (d) 10.0 wt%; the inset of UV-vis absorption edge of pure PANI.

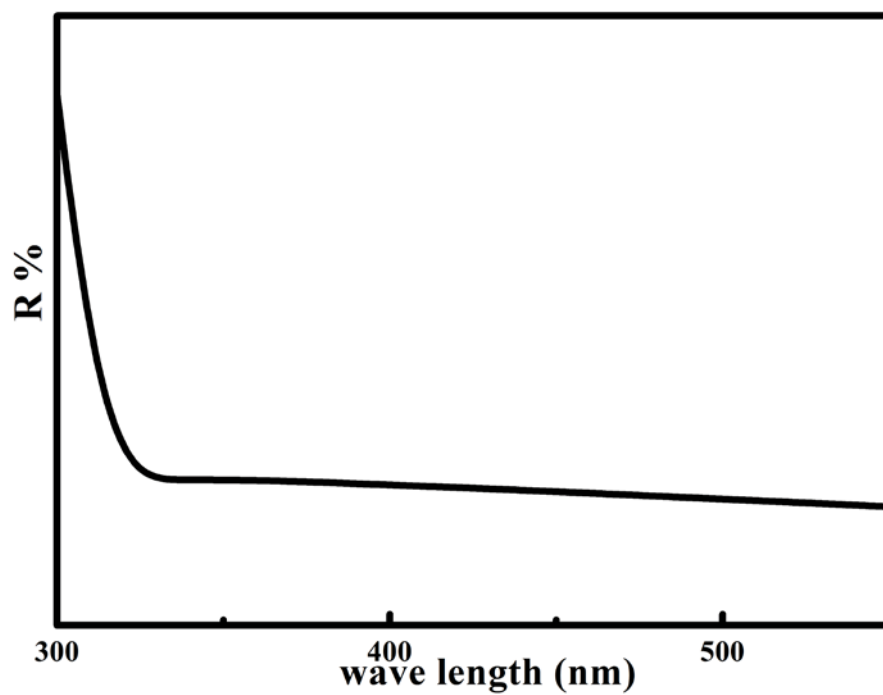


Figure 4.9 UV-Vis DRS of the as-received TiO₂ nanoparticles.

4.3.6 Optical properties

A band gap (E_g), also called energy gap, usually found in insulators and semiconductors, is correlated to the energy difference between the top of the valence band and the bottom of the conduction band.⁴⁵ The valence band is the highest occupied band (i.e., highest occupied molecular orbital, HOMO, for a molecule, while the conduction band is the lowest unoccupied band (i.e., the lowest unoccupied molecular orbital, LUMO, for a molecule).^{1, 46} A large exciton binding energy $E_g - E_g^{\text{opt}}$ (the difference between E_g and E_g^{opt} , where E_g^{opt} is the optical band gap), is commonly observed in organic materials, indicating that the E_g is larger than E_g^{opt} . However, for the inorganic materials, the $E_g - E_g^{\text{opt}}$ is small, which means that the E_g is almost equal to E_g^{opt} .¹ Two methods including inverse photoelectron spectroscopy (IPES) and ultraviolet photoelectron spectroscopy (UPS) can be utilized to measure the energy band gap.⁴⁵ Here, the UV-vis absorption edge (λ_{edge}) of pure PANI and its TiO_2 nanocomposites was characterized by using the UV-vis DRS method. the E_g^{opt} is calculated as equation 2.⁴⁷

$$E_g^{\text{opt}}(\text{eV}) = 1240 / \lambda_{\text{edge}}(\text{nm}) \quad (2)$$

The constant 1240 was derived from equation 3:

$$E(\text{eV}) = h\nu = h \frac{c}{e\lambda} \quad (3)$$

The equation 3 describes the relationship between frequency and wavelength, where, the Planck's constant is indicated by h , the speed of light in the vacuum is indicated by c with a value of $\sim 3 \times 10^8 \text{ m s}^{-1}$, and the electron charge is indicated by e , When converting the

Table 4.1 Absorption edge and optical band gap of pure PANI and TiO₂/PANI with a TiO₂ nanoparticle loading of 2.0, 5.0, and 10.0 wt%.

Samples	Absorption Edge of PANI (λ_{edge} , nm)	Optical band gap of PANI ($E_{\text{g}}^{\text{opt}}$, eV)
Pure PANI	392	3.16
2.0 wt% TiO ₂ / PANI	396	3.13
5.0 wt% TiO ₂ / PANI	391	3.17
10.0 wt% TiO ₂ / PANI	393	3.16

unit of λ from meter (m) to nanometer (nm), the constant 1240 can be derived from hc/e . The λ_{edge} of pure PANI and its TiO₂ nanocomposites is related to the π - π^* transition in the benzoid/quinoid structure of PANI. The λ_{edge} of pure PANI is determined by using the inset of the UV-vis DRS plot, **Figure 4.8**. The adsorption edge and optical band gap of pure PANI and its TiO₂ nanocomposites loaded with 2.0, 5.0 and 10.0 wt% TiO₂ nanoparticles are summarized in **Table 4.1**. However, there is no absorption for pure TiO₂ at the range from 300 to 550 nm in **Figure 4.9**. Therefore, only the absorption of PANI is observed in TiO₂/PANI nanocomposites. Compared with pure PANI, the $E_{\text{g}}^{\text{opt}}$ of the nanocomposites with different TiO₂ nanoparticles loadings is almost the same, indicating that the adding of TiO₂ nanoparticles into the PANI matrix has little effect on the $E_{\text{g}}^{\text{opt}}$ of PANI. The same result has also been observed in the Fe₃O₄/polypyrrole and Si/PANI nanocomposites.^{1, 5}

4.3.7 Mechanism of electrical conduction: temperature dependent resistivity

Figure 4.10 shows the temperature dependent resistivity of pure PANI and its TiO₂ nanocomposites loaded with 2.0, 5.0 and 10.0 wt% TiO₂ nanoparticles. For nanocomposite samples with different loadings of TiO₂ nanoparticles, **Figure 4.10A** demonstrates that the resistivity decreases with increasing the temperature, indicating the typical behavior of a semiconductor between 50 and 250 K.¹ The resistivity of the nanocomposites containing 2.0 wt% TiO₂/PANI is lower than that of pure PANI, which may be attributed to the fact that the in-situ grown PANI chains could be more densely packed in the presence of the TiO₂ nanoparticles.¹³ For the TiO₂/PANI nanocomposites with higher nanoparticle loadings, i.e., 5.0 wt% TiO₂, the resistivity of the nanocomposites is much higher within the measured temperature range. Further increasing the TiO₂ nanoparticle loading to 10.0

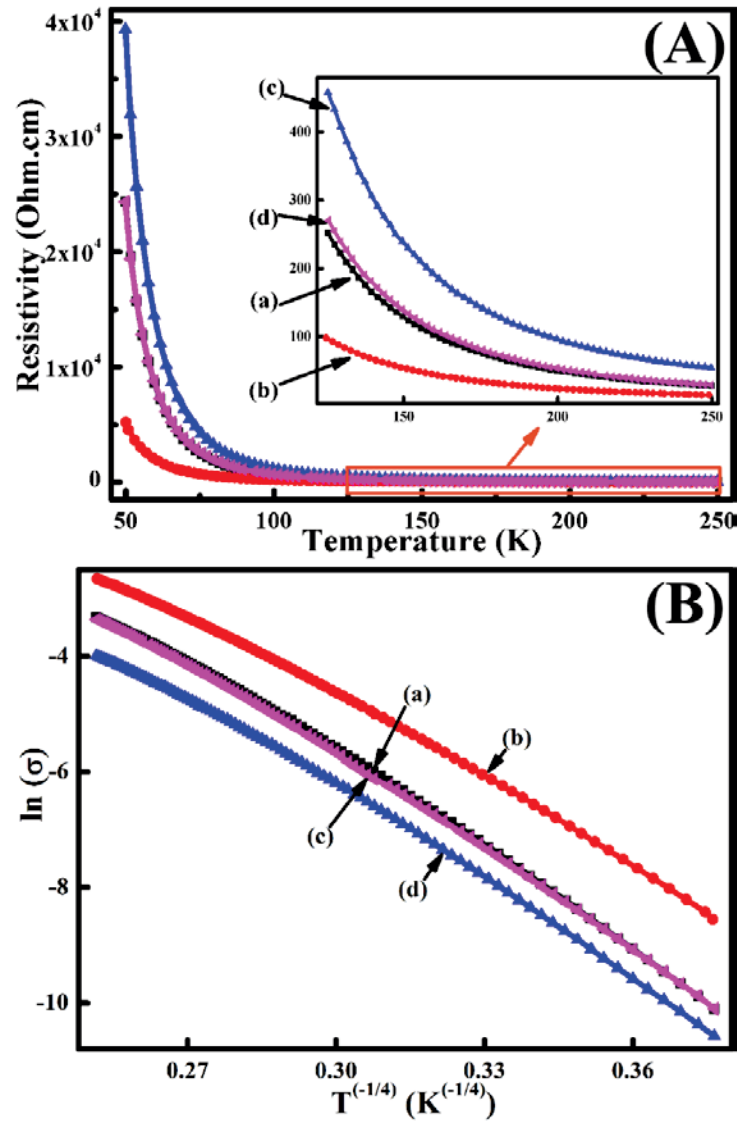


Figure 4.10 (A) Resistivity vs. temperature and (B) the $\ln(\sigma)$ vs. $T^{(-1/4)}$ curves of (a) pure PANI and TiO₂/PANI nanocomposites with a TiO₂ loading of (b) 2.0, (c) 5.0 and (d) 10.0 wt%, respectively.

wt% leads to a decrease in the resistivity, while it is still a little higher than that observed in pure PANI. For pure PANI, the resistivity decreases by about three orders of magnitude from 2.4×10^4 to $28.0 \Omega \cdot \text{cm}$ within the measured temperature (50 to 250 K). However, the resistivity of TiO_2/PANI nanocomposites with 2.0 wt% TiO_2 loading decreases significantly from 5.2×10^3 to $14.3 \Omega \cdot \text{cm}$ at 50 and 250 K, respectively. The 5.0 wt% TiO_2/PANI nanocomposites show the highest resistivity (about $3.9 \times 10^4 \Omega \cdot \text{cm}$ at 50 K, and $54.2 \Omega \cdot \text{cm}$ at 250 K). All these results indicate that the TiO_2 nanoparticles exert a significant impact on the resistivity of pure PANI, leading to the observed changes in the resistivity of the TiO_2/PANI nanocomposites. The value of the resistivity ratio ($\rho_r = \rho_{50}/\rho_{250}$) is further utilized to understand the disorder in pure PANI and its nanocomposites. Such disorder originates from the random potential fluctuation of quantum-well structures in the semiconductor,⁴⁸ which, for PANI, refers to the randomness in the sequence of quinoid-benzenoid groups in the PANI chains.⁴⁹ From the calculated ρ_r results summarized in **Table 4.2**, the ρ_r value for pure PANI is higher than that calculated for the TiO_2/PANI nanocomposites, indicating a larger disorder of pure PANI. For the TiO_2/PANI nanocomposites, an increase in the calculated ρ_r values was observed when the TiO_2 nanoparticle loading was increased, suggesting that the degree of disorder in the TiO_2/PANI nanocomposites is proportional to the TiO_2 nanoparticle loading.

The Mott variable range hopping (VRH) approach was further employed to investigate the electron transport behavior of pure PANI and its TiO_2 nanocomposites and to understand the electrical conduction mechanism. The low temperature resistivity in strongly disordered systems is described by equation. 4:²

Table 4.2 T_0 , σ_0 , and ρ_r for the Pure PANI, TiO₂/PANI nanocomposites with a TiO₂ nanoparticle loading of 2.0, 5.0 and 10.0 wt%.

Samples	$T_0 \times 10^6$ (K)	$\sigma_0 \times 10^4$ (S cm ⁻¹)	$\rho_r \times 10^2$
Pure PANI	8.10	2.95	8.73
2.0 wt%			
TiO ₂ /PANI	4.61	9.65	3.64
5.0 wt%			
TiO ₂ /PANI	7.29	1.07	7.25
10.0 wt%			
TiO ₂ /PANI	7.98	2.62	8.40

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/n} \right] \quad n=1, 2, 3 \quad (4)$$

where, σ_0 a pre-exponential factor and a constant represents the conductivity at an infinite low temperature limit, n values of 1, 2, and 3, correspond to one, two, and three dimensional systems, respectively,⁵⁰ and T is the temperature in Kelvin (K). In equation 4, T_0 represents the hopping barrier, i.e., the characteristic Mott temperature (K) and the energy required for charge carriers hopping. And T_0 can be further described in equation 5:²

$$T_0 = 24 / [\pi k_B N(E_F) a_0^3] \quad (5)$$

where, k_B , $N(E_F)$, and a_0 stands for the Boltzmann constant, the density of states at the fermi level, and the localization length of the localized charge carrier wave function, respectively.⁵¹ The equation 4 can be rearranged to equation 6:

$$\ln \sigma = \ln \sigma_0 - \left(\frac{T_0}{T} \right)^{1/n} \quad n=1, 2, 3 \quad (6)$$

Thus, σ_0 and T_0 can be extrapolated from the intercept and slope of the $\ln(\sigma)$ versus $T^{-1/(1+n)}$ plot, respectively. **Figure 4.10B** shows the calculated results from temperature dependent resistivity. Pure PANI and its TiO₂ nanocomposites with different TiO₂ loadings were found to follow the linear relationship of $\ln(\sigma) T^{-1/4}$, indicating a quasi 3-dimensional VRH mechanism. Therefore, the pure PANI and its TiO₂ nanocomposites are disordered systems in the 3-dimensional VRH regime. **Table 4.2** lists the σ_0 and T_0 values derived from **Figure 4.10B**. The calculated T_0 of pure PANI is greater than that of the TiO₂/PANI nanocomposites, which is in agreement with that observed in PANI nanorod with gold.⁵²

The obtained T_0 is proportional to the ρ_r for pure PANI and TiO₂/PANI nanocomposites. A larger T_0 , usually accompanied by an increased resistivity, suggests a stronger localization of the charge carriers.⁵³ While a smaller T_0 implies a weaker localization.⁵⁴ For the TiO₂/PANI nanocomposites, when the TiO₂ loading increased from 2.0 wt% to 5.0 wt%, the T_0 increased and the σ_0 decreased. However, when the TiO₂ nanoparticle loading increased from 5 to 10 wt%, the T_0 and σ_0 increased, owing to the modulated electromagnetic wave in the structured nanocomposites.

4.3.8 Magnetoresistance

The MR is calculated using equation 7:⁵⁵

$$\text{MR}\% = \frac{R(B) - R(0)}{R(0)} \times 100 \quad (7)$$

where $R(0)$ represents the resistance without magnetic field, and $R(B)$ is the resistance under a magnetic field B . In this study, the MR (at 290 and 130 K) was thoroughly evaluated for both pure PANI and its TiO₂ nanocomposites. **Figure 4.11&4.12** shows the MR values for pure PANI and its nanocomposites with 2.0 and 10.0 wt% TiO₂ nanoparticle loadings. A large negative MR is observed in all these samples at 290 K, Figure 11a. In comparison, a lower negative MR was observed at 130 K, **Figure 4.12**. Generally, the magnetic field sensor is based on the MR effect which can be used to represent the sensitivity of materials to magnetic field B . And the sensitivity can be expressed either by the MR values at low B magnetic field or linear with respect to B at low field.³ The slope at low magnetic field for PANI and TiO₂/PANI nanocomposites with 2.0 and 10.0 wt% nanoparticles is -7.59, -38.28 and -64.29, respectively. In our previous work, the slope of WO₃/PANI nanocomposites with 10.0 and 20.0 % WO₃ nanoparticles is 12.205 and 3.434,

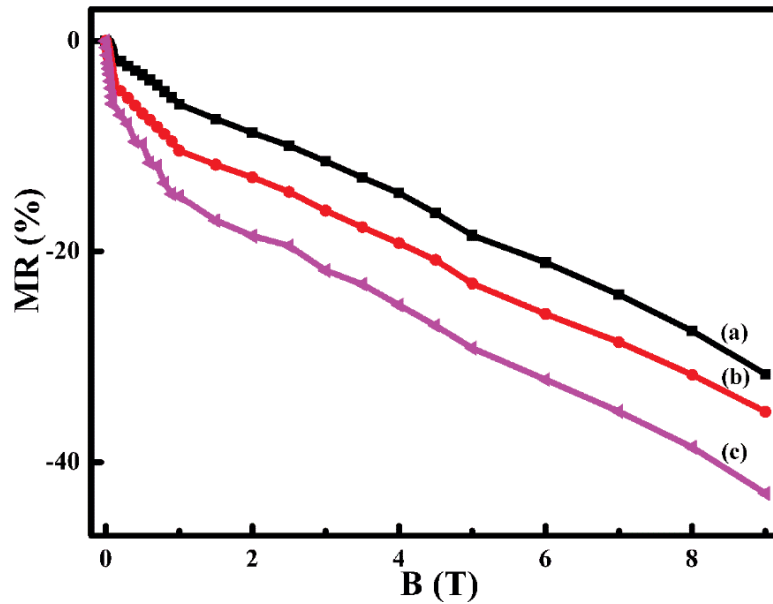


Figure 4.11 MR behavior of (a) pure PANI and TiO_2 /PANI nanocomposites with a TiO_2 nanoparticle loading of (b) 2.0, and (c) 10.0 wt% at 290 K.

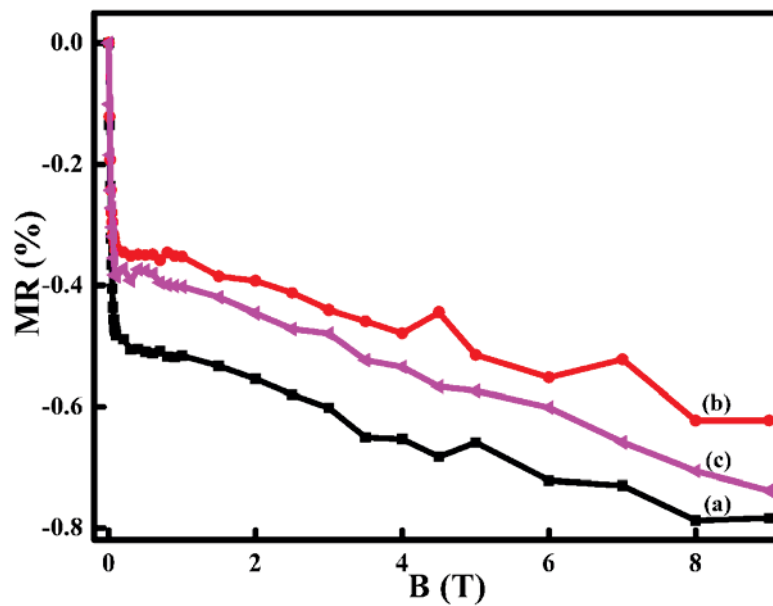


Figure 4.12 MR behavior of (a) pure PANI and TiO_2 /PANI nanocomposites with a TiO_2 nanoparticle loading of (b) 2.0, and (c) 10.0 wt% at 130 K.

respectively, and the slope for WO₃/polypyrrole nanocomposites with 40.0 and 60.0 % WO₃ nanoparticles is 14.351 and 18.213, respectively.³ The slope at 290 K of 5.0 wt% graphene/PANI, 5.0 wt% carbon nanofiber/PANI and 5.0 wt% carbon nanotubes/PANI nanocomposites is 36.95, and 114.80 and 54.57, respectively.¹⁰ The slope of 10.0 wt% TiO₂/PANI nanocomposites is higher than all the above samples except 5.0 wt% carbon nanofiber/PANI nanocomposites. The TiO₂/PANI nanocomposites shows enhanced MR sensitivity, and the MR values (0.5 T) for pure PANI, the nanocomposite with a 2.0 wt% nanoparticle loading, and the nanocomposites with a 10.0 wt% nanoparticle loading, are -3.233, -6.904 and -9.797% at 290 K, as well as -0.5091, -0.350 and -0.376% at 130 K, respectively. These results indicate that 10 wt% TiO₂/PANI nanocomposites display the highest sensitivity at 290 K, however, pure PANI shows the highest sensitivity at 130 K. It is worth noting that materials that exhibit a high MR sensitivity to an external magnetic field can be used as potential magnetic field sensors.⁵

The negative MR value was further evaluated using forward interference model, which is generally implemented by considering the effect of interference among various hopping paths. The hopping paths are composed of a sequence of scattering of tunneling electrons due to the impurities located within a cigar-shaped domain of length r_h (hopping distance) and width $(r_h a_0)^{1/2}$.¹ The $R(B,T)/R(0,T)$ ratio correlated to the interference effects can be described by an empirical equation.^{8,2}

$$R(B,T)/R(0,T) \approx 1/\{1 + C_{sat}[B/B_{sat}]/[1 + B/B_{sat}]\} \quad (8)$$

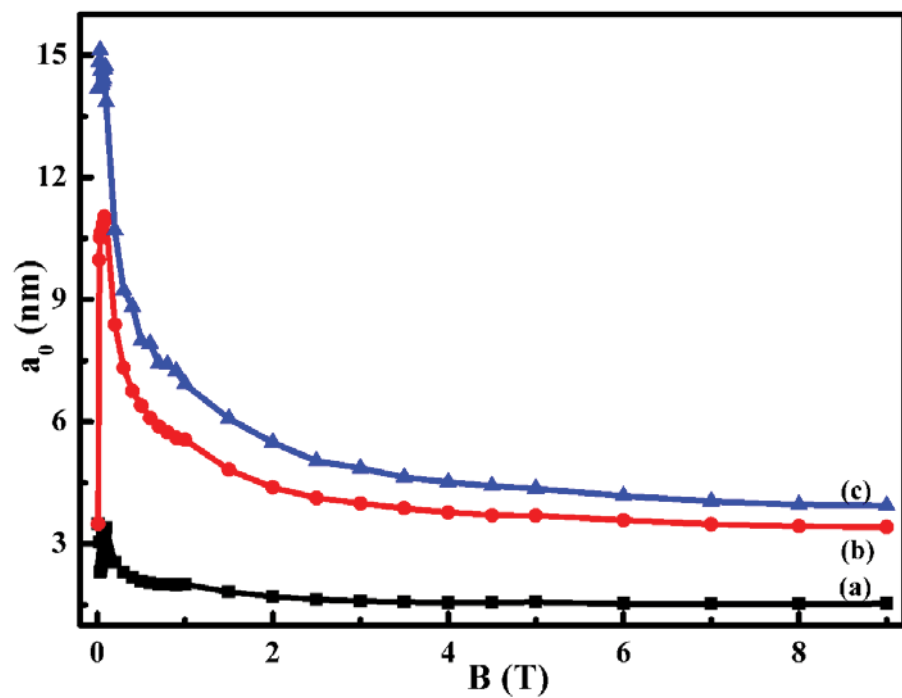


Figure 4.13 Magnetic field dependent localization length a_0 of (a) pure PANI and TiO_2/PANI nanocomposites with a TiO_2 nanoparticle loading of (b) 2.0, and (c) 10.0 wt% at 290 K.

where the fitting parameters C_{sat} is constant and B_{sat} is called effective saturation magnetic field. By fitting $R(B,T)/R(0,T) \sim H$ via equation 8 using Polymath software, the C_{sat} values thus obtained for the pure PANI and the nanocomposites with 2.0 and 10.0 % wt% TiO_2 loadings are 4.0865542, 0.9164445, and 0.8350201, respectively. Meanwhile, B_{sat} can be calculated by equation 9,⁵⁶ according to the Mott VRH electrical conduction mechanism.

$$B_{sat} \approx 0.7 \left(\frac{8}{3}\right)^{3/2} \left(\frac{1}{a_0^2}\right) \left(\frac{h}{e}\right) \left(\frac{T}{T_0}\right)^{3/8} \quad (9)$$

In equation 9, h indicates the Planck's constant, e is electron charge, and T_0 represents the Mott characteristic temperature (K). Furthermore, equation 8 can be simplified to equation 10, when the low-field limit is imposed:⁴⁴

$$R(B,T)/R(0,T) \approx 1 - C_{sat} [B/B_{sat}] \quad (10)$$

The MR values can be therefore calculated by substituting Equation 9 into equation 10, as described in equation 11:

$$MR = \frac{R(B,T) - R(0,T)}{R(0,T)} \approx -C_{sat} [B/B_{sat}] = -C_{sat} \frac{B}{0.7 \left(\frac{8}{3}\right)^{3/2} \left(\frac{1}{a_0^2}\right) \left(\frac{h}{e}\right) \left(\frac{T}{T_0}\right)^{3/8}} \quad (11)$$

The calculated a_0 values of pure PANI are 2.07, 2.00, 1.57 and 1.53 nm at B of 0.5, 1, 5 and 9 T, respectively. The calculated a_0 values for the nanocomposite with a 2.0 wt% TiO_2 loading are 6.40, 5.56, 3.70, and 3.40 nm at B of 0.5, 1, 5 and 9 T, respectively. When the TiO_2 loading is increased to 10.0 wt%, the calculated a_0 values are 7.98, 6.93, 4.35, and 3.94 nm at H of 0.5, 1, 5, and 9 T, respectively. The calculated a_0 values for both the pure PANI and its TiO_2 /PANI nanocomposites were further summarized in **Tables 4.3, 4.4&4.5**, and the relationship between localization length and magnetic field is

Table 4.3 Calculated localization length a_0 using the forward interference model for pure PANI.

Magnetic Field (T)	MR (%)	a_0 (nm)
8.999841	-31.6606	1.528116
7.999699	-27.5481	1.511901
6.999907	-24.101	1.511769
5.999821	-21.0538	1.526197
4.999985	-18.4803	1.566332
4.499808	-16.3789	1.554388
3.999964	-14.4684	1.549518
3.49989	-12.9787	1.568925
2.999866	-11.4453	1.591389
2.499955	-9.95872	1.62611
1.999922	-8.74066	1.703256
1.499801	-7.42957	1.81334
0.999947	-6.03061	2.000813
0.900031	-5.37544	1.991097
0.799992	-4.83642	2.003242
0.699996	-4.21526	1.999303
0.599994	-3.72278	2.029432
0.499995	-3.23302	2.071743
0.400002	-2.81946	2.163048
0.299989	-2.39199	2.300604
0.199991	-1.93087	2.531548
0.099994	-1.73017	3.389004
0.090008	-1.27702	3.068826
0.080026	-1.08743	3.003293
0.070012	-0.83285	2.810024
0.060017	-0.62403	2.627107
0.050003	-0.45185	2.449142
0.04003	-0.3297	2.338181
0.030049	-0.23908	2.298128
0.020016	-0.27771	3.034771
0.010024	-0.18411	3.491763

Table 4.4 Calculated localization length a_0 using the forward interference model for 2.0 wt% TiO₂/PANI nanocomposites.

Magnetic Field (T)	MR (%)	a_0 (nm)
8.999536	-35.2246	3.404306
7.99971	-31.7245	3.426697
6.999802	-28.6208	3.479473
5.999911	-25.9469	3.578377
4.999857	-23.0553	3.695063
4.499904	-20.8129	3.70067
4.000001	-19.2095	3.770884
3.499907	-17.7097	3.870729
2.999713	-16.1446	3.991985
2.500002	-14.3554	4.123379
1.999796	-12.9696	4.382134
1.500018	-11.7772	4.821563
0.999956	-10.4293	5.55717
0.900017	-9.53886	5.601942
0.799991	-8.86801	5.729099
0.699988	-8.18487	5.884052
0.599983	-7.52677	6.094674
0.500001	-6.90433	6.394272
0.399992	-6.15207	6.748397
0.300005	-5.43039	7.320938
0.200006	-4.75007	8.385792
0.099996	-4.07004	10.97798
0.090024	-3.67083	10.98798
0.079993	-3.28814	11.03225
0.070023	-2.7962	10.87375
0.060003	-2.33139	10.726
0.050013	-1.87644	10.53999
0.040008	-1.52855	10.63609
0.030008	-1.12145	10.51931
0.020018	-0.67244	9.973079
0.010012	-0.33889	3.491763

Table 4.5 Calculated localization length a_0 using the forward interference model for 10.0 wt% TiO₂/PANI nanocomposites.

Magnetic Field (T)	MR (%)	a_0 (nm)
8.999852	-42.9788	3.938491
8.00002	-38.6003	3.95886
7.000046	-35.2001	4.04149
5.99992	-32.1783	4.173776
4.999869	-29.1834	4.354202
4.49996	-27.0445	4.418304
3.999974	-25.1041	4.515068
3.499806	-23.1197	4.632225
2.999885	-21.8148	4.86008
2.499849	-19.4678	5.029461
1.999931	-18.5363	5.486857
1.499876	-17.0586	6.078047
0.999851	-14.7617	6.925012
0.900006	-14.5468	7.245707
0.799994	-13.4942	7.40203
0.699994	-11.8984	7.430478
0.599997	-11.5811	7.918097
0.499997	-9.79656	7.977618
0.400006	-9.58642	8.82298
0.299988	-7.85289	9.221111
0.199996	-7.05546	10.70464
0.100002	-5.91	13.8551
0.09001	-6.01586	14.73411
0.080003	-5.29836	14.66687
0.070005	-4.48227	14.4213
0.060017	-3.81207	14.3636
0.050019	-3.14027	14.28028
0.040033	-2.63743	14.62861
0.030044	-2.1173	15.12966
0.019989	-1.35516	14.83967
0.010003	-0.62009	14.1902

demonstrated in **Figure 4.13**. The above calculation results clearly demonstrate that the a_0 value has a trend to decrease with increasing the strength of the applied magnetic field. In addition, the MR value was found to decrease when increasing the TiO₂ nanoparticle loading from 2.0 to 10.0 wt%. Meanwhile, the calculated a_0 value of 2.0 wt% TiO₂/PANI nanocomposites is lower than that of 10.0 wt% TiO₂/PANI nanocomposites. Compared with the previous work, the PANI synthesized by the Cr (VI) as oxidant or doped by H₃PO₄ shows a different positive MR, and the a_0 is larger than that of the PANI we synthesized.^{5, 9, 44} The above observation suggests that the oxidant and doped acid show a significant effect on the MR behavior of PANI, and the H₃PO₄ doped PANI with positive MR shows larger a_0 than that of PANI with negative MR. However, It is interesting to find that the MR behavior of pure PANI is different with our previous work even with the same oxidant (APS) and doped acid (PTSA). The largest MR of PANI at 290 K is about 53% with aniline polymerization time 8 hours, the MR of PANI at 290 K could also be about 25% with aniline polymerization time 1 hour. And the synthesized PANI washed by methanol to remove the oligomer.^{2, 10, 13} In this work, the largest MR of PANI at 290K is -34% with aniline polymerization time 1.5 hour, and the PANI was not treated by methanol. When the MR measurement temperature changed from 290 to 130 K, the MR signal changed significantly. In summary, the polymerization time, oligomer and temperature has significant effect on the MR behavior.

4.4 Conclusion

The conductive TiO₂/PANI nanocomposites with various loadings were successfully synthesized through a facile SIP method. The results of SEM and HRTEM

show that the TiO₂ nanoparticles have been successfully embedded in conductive PANI matrix. The results from XRD indicate that the presence of TiO₂ nanoparticles exerts a significant influence on the crystallization of PANI. All the fabricated samples show a positive permittivity, which decreases with increasing the frequency within the measured frequency. The optical properties of TiO₂/PANI nanocomposites indicate that the adding of TiO₂ nanoparticles into the PANI matrix has little effect on the E_g^{opt} of PANI. The resistivity of pure PANI and its nanocomposites decreases with increasing the temperature, as observed in typical semiconductors. Mott VRH model was also used to understand the electrical conduction mechanism of the pure PANI and its TiO₂ nanocomposites. The results thus achieved suggest a quasi 3-*d* VRH mechanism for the TiO₂/PANI nanocomposite systems. A negative MR was also observed in pure PANI and its TiO₂ nanocomposites and the experimental results were discussed using the orbital magnetoconductivity theory. Overall, this study provides new insights into the enhanced negative magnetoresistance of the TiO₂/PANI nanocomposites, which were conveniently prepared using the SIP method.

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**Chapter 5. Significantly Enhanced Mechanical and Electrical Properties
of Epoxy Nanocomposites Reinforced with Low Loading of Polyaniline
Nanoparticles**

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Abstract

The polyaniline (PANI)/epoxy nanocomposites with enhanced mechanical and electrical properties were prepared by three different techniques. Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscope (SEM) were used to study the chemical structure and surface morphology of the PANI nanoparticles, which were synthesized by oxidation polymerization method. The effects of PANI loading and preparation method on the mechanical and electrical properties of PANI/epoxy nanocomposites were comparatively studied. The SEM images of the PANI/epoxy nanocomposites after doing the tensile test were used to study the dispersion of PANI nanoparticles in the epoxy matrix. The tensile strength of 5.0 wt% PANI/epoxy nanocomposites (107.27 MPa) was much higher than that of our previous PANI/epoxy nanocomposites (about 60.0 MPa) with the same PANI loading. The volume resistivity of the PANI/epoxy nanocomposites was also decreased compared to the reported literature. The toughness and Young's modulus of the PANI/epoxy nanocomposites were also studied and presented in this paper.

5.1 Introduction

Epoxy, considered as one of the most important engineered polymers, possesses a variety of high-technological applications, such as structural materials, flame retardant additives and anti-corrosion coating due to its high tensile strength, Young's modulus, good thermal and chemical resistance, and so on.¹⁻³ To make insulating epoxy (about 7.8×10^{13} ohm.cm) conductive, different conductive nanofillers including carbon nanofibers, iron nanoparticles and carbon coated iron (Fe@C) nanoparticles were added into the epoxy matrix to widen the applications of epoxy in other fields.⁴⁻⁸ These nanofillers could improve the electrical conductivity of epoxy, however, these nanofillers would damage the other properties of epoxy. For example, adding the conductive metal nanoparticles could improve the electrical conductivity, but it increases the weight of final epoxy finishing, which will challenge the requirement of the device and structure miniaturization.^{5, 9} The easy agglomeration of carbon nanofibers would reduce the mechanical property of the epoxy, and the surface treatment of the carbon nanofibers to improve the dispersion quality in the epoxy matrix would increase the cost for the fabrication of epoxy nanocomposites.^{10, 11}

Conductive polymers have attracted great attention due to their low cost, easy synthesis, flexibility, high capacitance and good environmental stability.¹² Among all the conductive polymers, polyaniline (PANI) is one of the most studied one because of its high conductivity, good stability, low cost, light weight, easy doping and de-doping, etc.^{5, 13} PANI could be applied in different fields including supercapacitors, environmental remediation and coupling agent between epoxy and nanofillers.^{13, 14} In our previous work,

the chemical bonding between PANI and epoxy has been formed and improved the mechanical property. After adding the PANI nanoparticles, the electrical conductivity of epoxy was increased without reducing other properties.^{5, 15} The dispersion quality of the nanoparticles in the epoxy matrix is a great challenge for enhancing the properties of the epoxy nanocomposites.⁵ In order to reach high quality dispersion, the nanofillers were mixed with epon resin under stirring, and the curing agent was added into the mixture for curing the epoxy nanocomposites. However, the fabrication procedure effect on the properties of cured epoxy nanocomposites has not been reported.

In this work, the PANI nanoparticles synthesized with an oxidation polymerization method were used as nanofillers to prepare epoxy nanocomposites with three different methods. The Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscope (SEM) were used to characterize the chemical structure, crystallization, and morphology of the synthesized PANI nanoparticles. The effects of fabrication procedure and PANI loading on the mechanical property and electrical conductivity were studied. To study the dispersion of PANI nanoparticles in the epoxy matrix, the fracture surface of the PANI/epoxy nanocomposites after doing the tensile test was studied by the SEM images as well.

5.2 Experimental

5.2.1 Materials

The epon 862 (bisphenol F epoxy) was provided by Miller-stephenson Chemical Company, Inc. Hexahydro-4-methylphthalic anhydride (98%) and acetone were obtained from Fisher Scientific. 2-ethyl-4-methylimidazole (EMI), aniline (C_6H_7N), ammonium

persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) and *p*-toluene sulfonic acid (PTSA, $\text{C}_7\text{H}_8\text{O}_3\text{S}$, $\geq 98.5\%$) were purchased from Sigma Aldrich. All the chemicals were used as-received without any further treatment.

5.2.2 Preparation of PANI nanoparticles

PANI nanoparticles were synthesized by oxidation polymerization method. Briefly, the molar ratio was aniline: APS: PTSA = 6:3:5. For solution 1, PTSA (30 mmol) and APS (18 mmol) were dissolved in deionized water (200 mL) in a beaker, which was treated by sonication (Branson 8510) in the ice water bath for 1 hour mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer 300 rpm). Solution 2 was aniline (36 mmol) dissolved in deionized water (50 mL). Solution 2 was then added into solution 1, and the mixture was sonicated for an additional 1.5 hour mechanical stirring (300 rpm) in the ice water bath for polymerization of aniline. Finally, the product was vacuum filtered and washed with deionized water and massive acetone for 3 times.

5.2.3 Preparation of PANI/epoxy nanocomposites with three different methods

In this project, we prepared the PANI/epoxy nanocomposites with three different methods to study the processing effect on mechanical and electrical properties of the epoxy nanocomposites. The following are details for the three methods to prepare PANI/epoxy nanocomposites.

a. “PANI/epoxy-1” method

After washed with acetone, the PANI product (0.4545g, or 2.3684g) was soaked with the hexahydro-4-methylphthalic anhydride (19.75g) in a beaker. In order to remove acetone, the solution was put into the vacuum oven for 1 hour at 40 °C, then the PANI

nanoparticles were immersed in hexahydro-4-methylphthalic anhydride without any disturbance overnight at room temperature. The solution was treated by sonication and mechanical stirring at 600 rpm for 1 hour at room temperature. Then the beaker was mechanically stirred at 200 rpm in a hot water bath at 80 °C. The epon monomer (25g) and 2-ethyl-4-methylimidazole (0.25g) were added into the beaker. Finally, after about 0.5 hour stirring, the solution was poured into the silicon rubber molds and cured at 100 °C for 3 hours, 140 °C for 4 hours and then cooled naturally to room temperature. The weight ratio was epon resin: hexahydro-4-methylphthalic anhydride: 2-ethyl-4-methylimidazole = 25g: 19.75g: 0.25g. The PANI/epoxy nanocomposites with 1.0 and 5.0 wt% PANI nanoparticles were synthesized by this method. The samples were named as 1.0 wt% PANI/epoxy-1 and 5.0 wt% PANI/epoxy-1, respectively.

b. “PANI/epoxy-2” method

After washed with acetone, the PANI product (0.4545g, or 2.3684g) was soaked with epon (25g) in a beaker. To remove acetone, the beaker was put into the vacuum oven for 1 hour at 40 °C. The PANI nanoparticles were immersed in epon without any disturbance overnight at room temperature. The solution was treated by sonication and mechanical stirring 600 rpm for 1 hour at room temperature. The solution was then heated to 80 °C in a hot water bath under mechanical stirring 200 rpm. Hexahydro-4-methylphthalic anhydride (19.75g) and 2-ethyl-4-methylimidazole (0.25g) were added and stirred for about 0.5 hour. The solution was then poured into the silicon rubber molds and cured at 100 °C for 3 hours, 140 °C for 4 hours and then cooled naturally to room temperature. The PANI/epoxy nanocomposites with 1.0 and 5.0 wt% PANI nanoparticles

were synthesized, respectively. The samples were named as 1.0 wt% PANI/epoxy-2, and 5.0 wt% PANI/epoxy-2, respectively.

c. “PANI/epoxy-3” method

After washed with acetone, the PANI product (0.4545g, 0.918g, 2.3684g or 3.9130g) was soaked with epon resin (25g) in a beaker. To remove acetone, the beaker was put into the vacuum oven for 1 hour at 40 °C. The PANI nanoparticles were immersed in epon resin without any disturbance overnight at room temperature. Hexahydro-4-methylphthalic anhydride (19.75g) was added into the solution. The solution was treated by sonication and mechanical stirring 600 rpm for 1 hour at room temperature. Then the solution was heated to 80 °C in a hot water bath under mechanical stirring 200 rpm. When the temperature was 80 °C, 2-ethyl-4-methylimidazole (0.25g) was added into the solution and stirred for about 0.5 hour. The mixture was poured into the silicon rubber molds and cured at 100 °C for 3 hours, 140 °C for 4 hours and then cooled naturally to room temperature. The PANI/epoxy nanocomposites with 1.0, 2.0, 5.0 and 8.0 wt% PANI nanoparticles were synthesized by this method. The samples were named as 1.0 wt% PANI/epoxy-3, 2.0 wt% PANI/epoxy-3, 5.0 wt% PANI/epoxy-3 and 8.0 wt% PANI/epoxy-3, respectively. The cured pure epoxy was also synthesized with the same method without adding the PANI nanoparticles.

5.2.4 FT-IR, XRD and SEM characterizations

The chemical structure of the synthesized PANI nanoparticles was analyzed by a Fourier transform infrared spectroscopy (FT-IR), coupled with an ATR accessory (Burker Vector 22) in the range of 500-4000 cm^{-1} with a resolution of 4 cm^{-1} . The XRD was

measured by D/max-rB wide-angle X-ray diffractometer at a Cu k_{α} wavelength of 0.154 nm. The morphologies of the synthesized PANI nanoparticles and the fracture surface of the cured pure epoxy and PANI/epoxy nanocomposites were examined by a Hitachi S4300 scanning electron microscopy (SEM). All the samples were sputter coated a thin layer of gold (about 5 nm) to ensure good imaging.

5.2.5 Mechanical properties

Tensile test was carried out following ASTM, D412-98a in a unidirectional tensile test machine (ADMET tensile strength testing system 2610). The parameters (displacement and force) were controlled by a digital controller (MTESTQuattro) with MTESTQuattro Materials Testing Software. The samples (dog-bone shaped) were designed according to the ASTM standard requirement and prepared as described for the epoxy nanocomposites in the molds. A crosshead speed of 1 mm/min was used and the strain (mm/mm) was calculated by dividing the jogging displacement by the original gauge length. For each loading sample, we made 5 dog-bone, and did the tensile test to get the average data.

5.2.6 Volume resistivity

The volume resistivity, which is the inverse of electrical conductivity, was measured by testing the DC resistance along the disc samples with a diameter of about 60 mm with an Agilent 4339B high resistance meter (with the resistivity measurement up to $10^{16} \Omega \text{ cm}$) and by a four-probe technique (C4S 4-Point Probe Head Cascade Microtech., the probe tips were made of tungsten carbide). For each loading sample, we measured the volume resistivity 5 times, then get the average data.

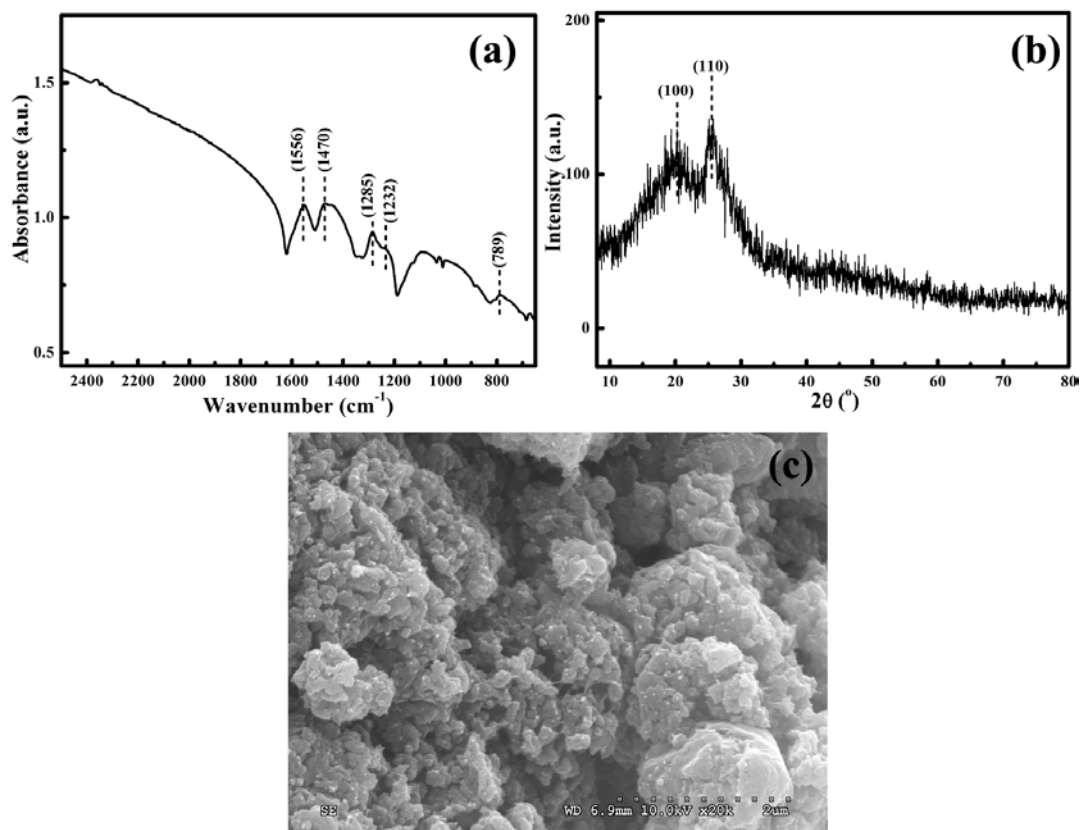


Figure 5.1 (a) FT-IR spectrum, (b) XRD pattern and (c) SEM microstructures of the synthesized PANI nanoparticles.

5.3 Results and discussions

Figure 5.1(a) shows the FT-IR spectrum of PANI nanoparticles. The peaks at 1556 and 1470 cm^{-1} correspond to the C=C stretching vibration of the quinoid and benzenoid rings of the PANI polymer backbone, respectively.¹⁶ The peak at 1285 cm^{-1} is due to the C-N stretching vibration of the benzenoid unit, and the peak around at 1232 cm^{-1} is assigned to the C-H stretching vibration of the quinoid rings.¹⁷ The peak at 789 cm^{-1} corresponds to the out-of-plane bending of C-H in the substituted benzenoid ring. These prove that the PANI nanoparticles are the emeraldine salt form.¹² The two broad diffraction peaks at $2\theta = 20.1$ and 25.3° , **Figure 5.1(b)**, correspond to the (100) and (110) crystallographic plane of the partially crystalline PANI nanoparticles.¹⁷ **Figure 5.1(c)** shows the SEM image of the PANI nanoparticles. The PANI nanoparticles have a rough surface with an average diameter of 110 nm measured by the nano measurer software. All the results indicate that the PANI nanoparticles have been successfully synthesized.

Figure 5.2 shows the curve of tensile stress as a function of tensile strain for the cured pure epoxy and PANI/epoxy nanocomposites with different fabrication methods. The tensile strength of cured pure epoxy is 80.87 MPa, a little lower than that of pure epoxy with curing agent Epicure W.² The PANI/epoxy nanocomposites with a PANI loading of 5.0 wt% show an enhanced tensile strength compared with that of cured pure epoxy, which is due to the covalent bondings formed between PANI nanoparticles and epoxy matrix.^{15,}
¹⁸ And the PANI/epoxy-3 nanocomposites show much higher tensile strength (107.27 MPa) than PANI/epoxy-2 (96.35 MPa) and PANI/epoxy-1 (88.81 MPa). However, the tensile strength of 8.0 wt% PANI/epoxy-3 nanocomposites was decreased to 62.93 MPa,

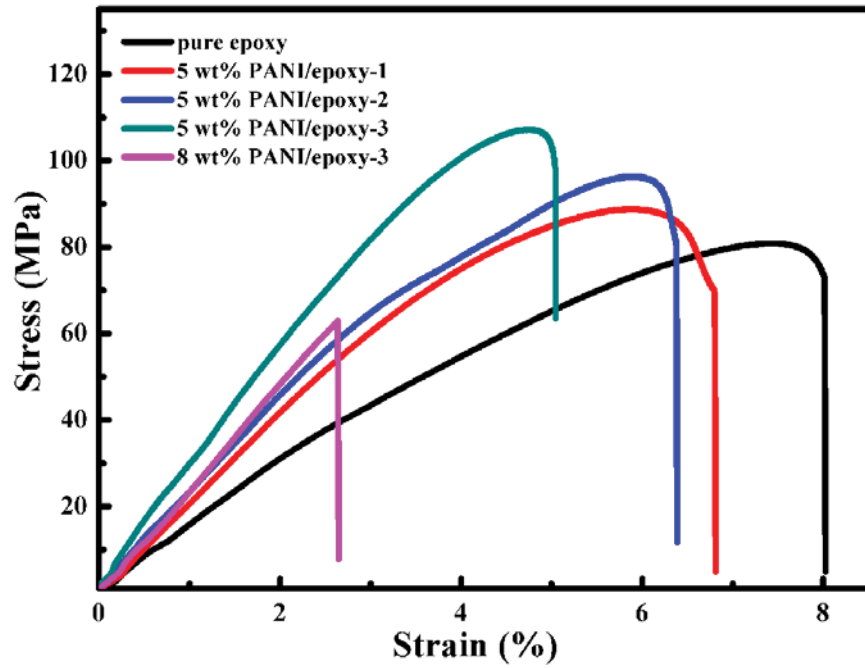


Figure 5.2 Stress-strain curves of cured pure epoxy, 5.0 wt% PANI/epoxy-1, 5.0 wt% PANI/epoxy-2, 5.0 wt% PANI/epoxy-3, and 8.0 wt% PANI/epoxy-3, respectively.

Table 5.1 Young's modules and toughness of pure epoxy and PANI /epoxy nanocomposites.

	Toughness ($\text{J} \cdot \text{m}^{-3} \cdot 10^4$)	Young's modulus (GPa)
Pure epoxy	406.0	1.6
5.0 wt% PANI/epoxy-1	395.0	2.2
5.0 wt% PANI/epoxy-2	387.0	2.3
5.0 wt% PANI/epoxy-3	331.0	3.1
8.0 wt% PANI/epoxy-3	83.0	2.6

which is induced by the agglomeration of the PANI nanoparticles.⁵ The young's modulus is the slope of the stress-strain curve at elastic portion. And the toughness can be determined by integrating the stress-strain curve. The young's modules and toughness of pure epoxy and PANI/epoxy nanocomposites are summarized in **Table 5.1**. Adding the PANI nanoparticles into the epoxy matrix would reduce the toughness of epoxy but enhance the young's modulus of the epoxy. These results indicate that the stiffness is improved by sacrificing the toughness, which is consistent with the results in magnetic epoxy nanocomposites and layered silicates/epoxy nanocomposites.^{19, 20}

Figure 5.3 shows the SEM images of the fracture surface of the cured pure epoxy and PANI/epoxy nanocomposites with different synthesized methods and PANI loadings. A relatively smooth fracture surface with “river-like” patterns is observed in the SEM images of pure epoxy, **Figure 5.3(a)**, indicating a brittle failure because of the rapid crack propagation.²¹ Adding the PANI nanoparticles into the epoxy matrix, the fracture surface of the PANI/epoxy nanocomposites becomes much rougher, **Figure. 5.3(b, c, d&e)**. However, compared with 5.0 wt% PANI/epoxy-1 and 5.0 wt% PANI/epoxy-2 nanocomposites, **Figure 5.3(b&c)**, the fracture surface of 5.0 wt% PANI/epoxy-3 nanocomposites is relatively smoother, indicating that the PANI nanoparticles have a good dispersion in the epoxy matrix, **Figure 5.3d**. Due to the good nanoparticle dispersion in the epoxy matrix and the covalent bondings formed between PANI nanoparticles and epoxy matrix,¹⁸ the tensile strength (107.27 MPa) of 5.0 wt% PANI/epoxy-3 nanocomposites is much higher than previous reported PANI/epoxy nanocomposites (about 60.0 MPa) at the same PANI loading.⁵ The agglomeration of the PANI nanoparticles

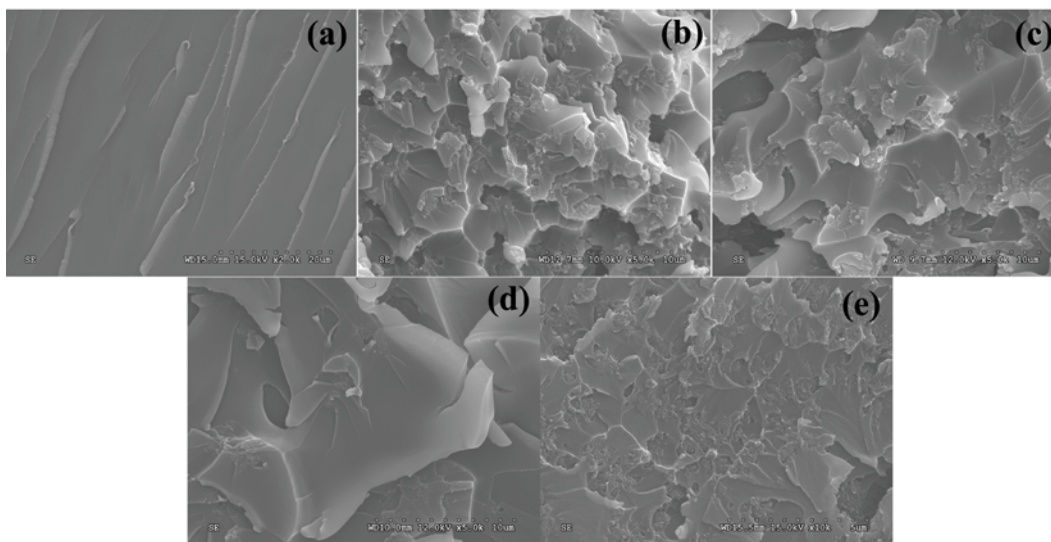


Figure 5.3 SEM microstructures of the fracture surface of (a) cured pure epoxy, 5.0 wt% PANI/epoxy nanocomposites synthesized by (b) “5.0 wt% PANI/epoxy-1”, (c) “5.0 wt% PANI/epoxy-2”, and (d) “5.0 wt% PANI/epoxy-3”, and (e) 8.0 wt% PANI/epoxy-3, respectively.

is observed in the fracture surface of 8.0 wt% PANI/epoxy-3 nanocomposites, **Figure 5.3e**, and leads to a decreased tensile strength (62.93 MPa). However, the 8.0 wt% PANI/epoxy-3 nanocomposites still shows higher tensile strength (62.93 MPa) than previous reported PANI nanocomposites with 10.0 wt% PANI loading (about 55 MPa).⁵

Figure 5.4 depicts the volume resistivity of the cured pure epoxy and its PANI nanocomposites with different fabrication methods. The volume resistivity of cured pure epoxy is about $1.1629 \times 10^{16} \Omega \text{ cm}$. The volume resistivity is decreased by adding the conductive PANI nanoparticles into the epoxy matrix. When the PANI loading is 5.0 wt%, the volume resistivity of the nanocomposites is decreased to $2.06785 \times 10^{12} \Omega \text{ cm}$ for PANI/epoxy-1 nanocomposites, $2.3913 \times 10^{12} \Omega \text{ cm}$ for PANI/epoxy-2 nanocomposites. However, for the 5.0 wt% PANI/epoxy-3 nanocomposites, the volume resistivity is decreased to $3.0928 \times 10^{11} \Omega \text{ cm}$, indicating that the PANI nanoparticles are well dispersed in the epoxy matrix, which is consistent with the SEM observation of the fracture surface of PANI/epoxy nanocomposites. When increasing the PANI loading to 8.0 wt%, the volume resistivity PANI/epoxy-3 nanocomposites was decreased to $3.8017 \times 10^{10} \Omega \text{ cm}$, even lower than that of our previous reported PANI/epoxy nanocomposites with 10.0 wt% PANI nanoparticles (about $1.0 \times 10^{11} \Omega \text{ cm}$).⁵ **Figure 5.5** depicts the volume resistivity of PANI/epoxy-3 nanocomposites with different PANI nanoparticle loadings. When 1.0 and 2.0 wt% PANI nanoparticles were added into the epoxy matrix, the volume resistivity were decreased to 1.5576×10^{14} , and $1.31943 \times 10^{14} \Omega \text{ cm}$ for 1.0 wt% PANI/epoxy-3, and 2.0 wt% PANI/epoxy-3 nanocomposites, respectively. However, when the PANI loading was increased to 5.0 wt%, the volume resistivity of 5.0 wt% PANI/epoxy-3 nanocomposites

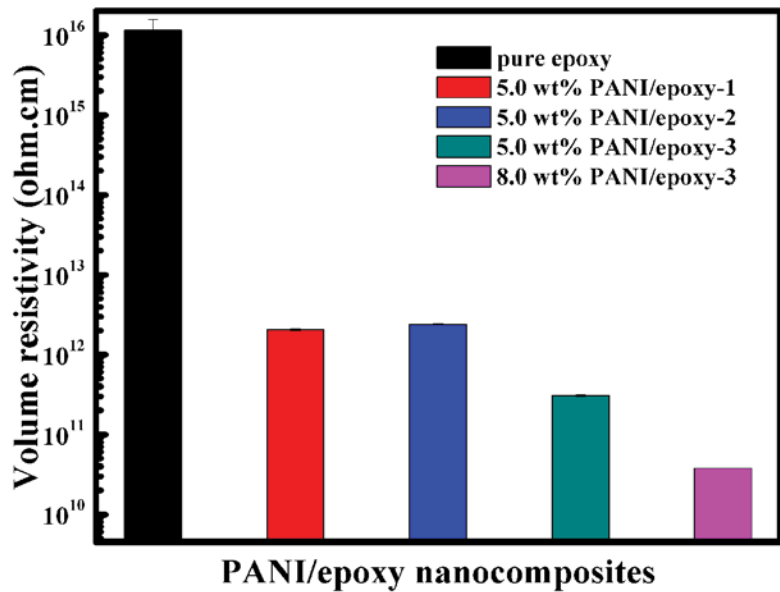


Figure 5.4 Volume resistivity of pure epoxy, 5.0 wt% PANI/epoxy-1, 5.0 wt% PANI/epoxy-2, 5.0 wt% PANI/epoxy-3, and 8.0 wt% PANI/epoxy-3, respectively.

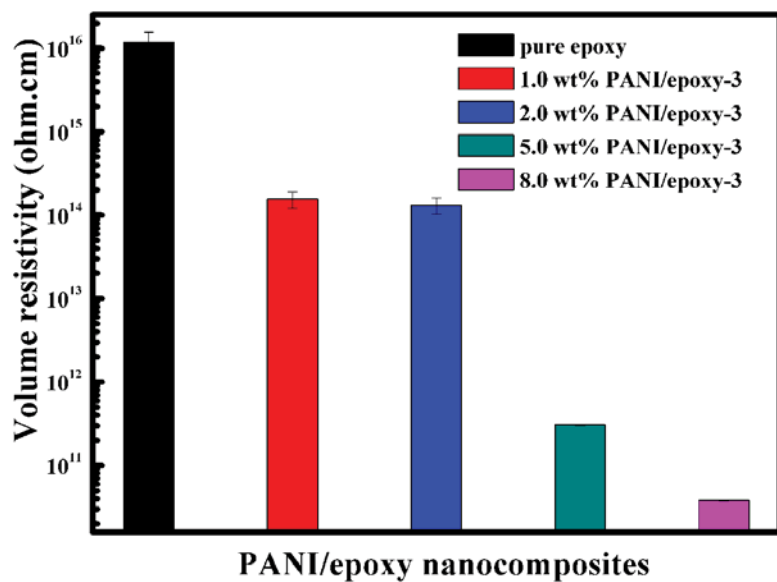


Figure 5.5 Volume resistivity of pure epoxy, 1.0 wt% PANI/epoxy-3, 2.0 wt% PANI/epoxy-3, 5.0 wt% PANI/epoxy-3, and 8.0 wt% PANI/epoxy-3, respectively.

was decreased significantly, almost 4 orders of magnitude lower than that of the cured pure epoxy ($1.1629 \times 10^{16} \Omega \text{ cm}$). The variation of volume resistivity of the PANI/epoxy-3 nanocomposites with different loadings of PANI nanoparticles indicated the formation of percolated network. At lower PANI loading, the PANI nanoparticles rarely contact to each other, which makes the electron hopping more difficult because of the large spacing between particles.²² When the particle loading was increased to higher percent, the percolation network was formed by nanoparticles in the epoxy matrix at a certain nanoparticle loading, making the electron hopping much easier between neighboring nanoparticles.²³ Similar phenomenon is also observed the epoxy nanocomposites with iron-core-carbon-shell nanoparticles.⁴

5.4 Conclusion

The PANI nanoparticles prepared with oxidation polymerization method have been successfully prepared as fillers for epoxy nanocomposites with three different approaches. The PANI nanoparticles have a good dispersion in the epoxy matrix, which is observed in the SEM result of fracture surface of the PANI/epoxy nanocomposites after doing the tensile test. Compared with PANI/epoxy-1 and PANI/epoxy-2 nanocomposites, the PANI/epoxy-3 nanocomposites showed better electrical conductivity ($3.0928 \times 10^{11} \Omega \text{ cm}$) and mechanical property (107.27 MPa), indicating that the synthesized process has a significant effect on the properties of PANI/epoxy nanocomposites. Both electrical conductivity and mechanical property (tensile strength) were significantly enhanced at 5.0 wt% PANI loading, compared with pure epoxy ($1.1629 \times 10^{16} \Omega \text{ cm}$ and 80.87 MPa). And 8.0 wt% PANI/epoxy-3 nanocomposites showed better electrical conductivity

($3.8017 \times 10^{10} \Omega \text{ cm}$) and mechanical property (tensile strength 62.93 MPa) than previous reported PANI/epoxy nanocomposites with 10.0 wt% PANI loading ($1.0 \times 10^{11} \Omega \text{ cm}$ and 55.0 MPa). Adding the PANI nanoparticles into the epoxy matrix could increase the Young's modulus of the epoxy, but decrease the toughness of the epoxy.

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**Chapter 6. Polypyrrole-Interface-Functionalized Nano-magnetite Epoxy
Nanocomposites as Electromagnetic Wave Absorber with Enhanced
Flame Retardancy**

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Abstract

Epoxy nanocomposites reinforced with polypyrrole functionalized nano-magnetite (Fe_3O_4 -PPy) showed significantly enhanced electromagnetic wave absorption performance and flame retardancy. The Fe_3O_4 -PPy were prepared by the surface initiated polymerization method. The epoxy/(30.0wt%) Fe_3O_4 -PPy nanocomposites possess a minimum reflection loss (RL) value of -35.7 dB, which is much lower than that of either epoxy/(7.5wt%)PPy nanocomposites with a minimum RL value of -11.0 dB or epoxy/(30.0wt%) Fe_3O_4 with a minimum RL value of -17.8 dB at the same thickness (1.7 mm). Meanwhile, the bandwidth of epoxy/(30.0wt%) Fe_3O_4 -PPy nanocomposites for $\text{RL} < -10$ dB and $\text{RL} < -20$ dB is 4.0 GHz and 0.8 GHz, respectively. The increased interface area, eddy current loss and anisotropic energy are essentially important to acquire higher reflection loss and broader absorption bandwidth for epoxy/(30.0wt%) Fe_3O_4 -PPy nanocomposites. Moreover, the significantly reduced flammability was observed in the epoxy/(30.0 wt%) Fe_3O_4 -PPy nanocomposites compared with pure epoxy. The total heat release of epoxy/(30.0 wt%) Fe_3O_4 -PPy decreased from 25.5 kJ/g of pure epoxy to just 12.3 kJ/g. The tensile strength of the epoxy nanocomposites was reported as well.

6.1 Introduction

Nowadays, due to the rapid development of information technology, the electronic devices have been widely used for commercial and military applications.^{1, 2} The electromagnetic waves have been deployed in wireless cell phones, local area networks and other communication facilities.³ However, usage of electronic devices usually lead to serious electromagnetic wave interference (EMI) problems.⁴ Human beings have paid much attention to this problem because of the harmful effect of electromagnetic radiation.⁵ Therefore, suitable electromagnetic wave absorption materials are urgently needed. In recent years, polymer nanocomposites have been widely studied due to their cost-effective process ability, light weight, enhanced mechanical property and unique physiochemical properties.⁶⁻¹⁵ Polymer nanocomposites are one of the best materials for electromagnetic wave absorption in a wide absorption frequency range.¹⁶⁻¹⁸ Epoxy resin, as a typical engineering thermosetting material, has been widely used in industry for various applications such as coating and adhesives, due to the high Young's modulus, chemical resistance, and good thermal stability.^{7, 19-24} In order to widen the application of epoxy resin for EMI shielding application, different nanofillers were added. For example, Liang *et al.* synthesized the graphene epoxy nanocomposites with enhanced EMI shielding performance.¹ Kim *et al.* reported the nickel coated multi-wall carbon nanotubes epoxy nanocomposites with increased EMI shielding efficiency.²⁵

The electrical conductive polypyrrole (PPy) has been widely studied for various applications such as biosensors, membranes, coating materials, energy storage, photovoltaic cells and EMI shielding, because of its low cost, easy preparation, high yield

and excellent electrical property.²⁶⁻³⁰ Recently, the PPy based nanocomposites for EMI shielding have been reported. For example, Kim *et al.* synthesized PPy–nylon 6 composite fabrics in which EMI shielding efficiency was dependent on the electrical conductivity and layer array sequence.³¹ Avlani *et al.* studied the PPy-coated polyester nonwoven textiles, and these composites with low surface electrical conductivity showed a better EMI shielding efficiency.³² Although PPy has some advantages for EMI shielding application, there are two shortcomings. First, as non-magnetic material, only the dielectric loss can affect EMI shielding performance. Second, the dielectric permittivity and magnetic permeability are out of balance for PPy, resulting in a bad impedance matching. In order to overcome these defects, the magnetic nanoparticles are needed. Among all the magnetic materials, magnetite (Fe_3O_4) is widely used because of its magnetic property, low toxicity, high biocompatibility and high Snoek's limit.³ In recent years, much work has been carried out on EMI shielding performance of conductive polymer nanocomposites. For example, Wang *et al.* reported the cobalt/PPy nanocomposites with tunable electromagnetic properties because of the coexistence of magnetic loss and dielectric loss of electromagnetic waves.³³ Sun *et al.* reported the magnetic graphene with good EMI shielding performance.³ However, there is less work on the EMI shielding property of PPy with Fe_3O_4 nanocomposites. In our previous work, the Fe_3O_4 nanoparticles coated with PPy have been successfully synthesized by the surface initial polymerization (SIP) method.²⁶ The PPy functionalized Fe_3O_4 nanoparticles (PPy- Fe_3O_4) show enhanced dielectric, electrical and magnetic properties, indicating the materials may have potential for EMI shielding application. In addition, it is well known that the electromagnetic

energy is transformed to joule thermal energy by the EMI shielding materials. The generated joule thermal energy has the potential to ignite the materials. Thus, the flame retardant property is a vital parameter for the EMI shielding materials in the practical applications. Conductive polymer has shown its great potential as the flame retardant materials. For example, Zhang *et al.* reported the PPy epoxy nanocomposites with reduced flammability.³⁴ Gu *et al.* reported the enhanced flame retardancy performance of the epoxy nanocomposites with polyaniline stabilized silica nanoparticles.³⁵ Therefore, the PPy could enhance the flame retardant property of the epoxy nanocomposites as well. Especially, as mentioned above, there is less work done about the epoxy nanocomposites with PPy-Fe₃O₄ nanoparticles.

Herein, epoxy nanocomposites with Fe₃O₄-PPy nanoparticles have been reported with a higher electromagnetic wave absorption capacity and broader absorption bandwidth at high frequency compared to epoxy nanocomposites with PPy, Fe₃O₄, and the two physically mixed fillers (PPy and Fe₃O₄). A scanning electron microscopy was used to study the dispersion quality of the nanoparticles in the epoxy matrix. The electrical conductivity, magnetic property and electromagnetic wave absorption property were comparatively studied. In addition, the flame retardant property was evaluated by the microscale combustion calorimetry to satisfy stringent industrial standards.

6.2 Experimental

6.2.1 Materials

The bisphenol F epoxy (Epon 862) and curing agent (EpiCure W) were provided by Miller-Stephenson Chemical Company, Inc. Pyrrole (C₄H₅N, ≥ 98%), ammonium

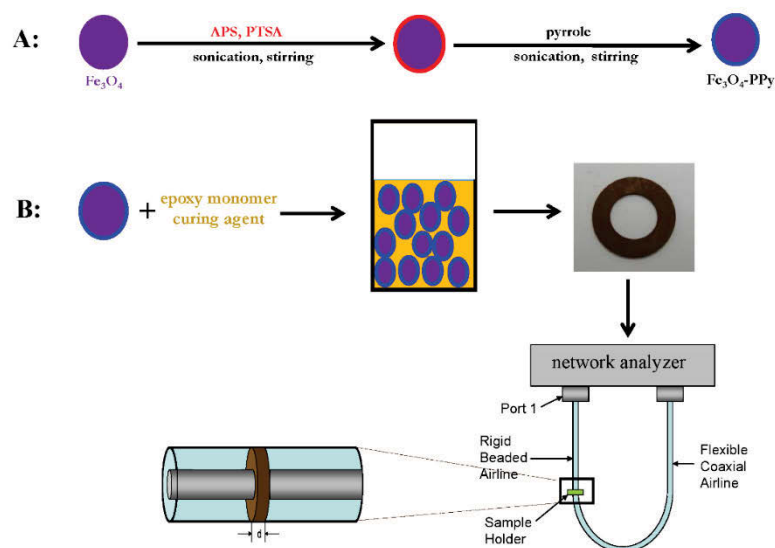


Figure 6.1 Process for the fabrication of (A) PPy functionalized Fe₃O₄ nanoparticles, (B) epoxy Fe₃O₄/PPy nanocomposites and the measurement of electromagnetic wave absorption property.

persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98%) and *p*-toluene sulfonic acid (PTSA, $\text{C}_7\text{H}_8\text{O}_3\text{S}$, $\geq 98.5\%$) were purchased from Sigma-Aldrich. The Fe_3O_4 nanoparticles were obtained from Nanjing Emperor Nano Material Co., Ltd., China. All the chemicals were used as-received without any further treatment.

6.2.2 Synthesis of cured epoxy nanocomposites

The preparation of cured pure epoxy and epoxy nanocomposites with 5.0, 20.0, 30.0 wt% Fe_3O_4 -PPy and 30.0 wt% as-received Fe_3O_4 nanoparticles were conducted. The SIP method for the surface functionalization of Fe_3O_4 nanoparticles by PPy was used,²⁶ as shown in **Figure 6.1 (A)**. First, the Fe_3O_4 nanoparticles were dispersed in an aqueous solution containing PTSA (15 mmol) and APS (9 mmol) in 100 mL of deionized water by sonication 1 hour and mechanical stirring in an ice-water bath. Second, the pyrrole solution (18 mmol, 25 mL deionized water) was mixed with Fe_3O_4 nanoparticles suspension for polymerization under mechanically and ultrasonically stirring for an additional one and half hours in an ice-water bath. The product was filtered and washed with deionized water several times. The epoxy nanocomposites with a physical mixture of 7.5 wt% PPy and 30.0 wt% as-received Fe_3O_4 nanoparticles, epoxy nanocomposites with 7.5 wt% PPy were also prepared in this work.^{7, 26} Here, the epoxy nanocomposites with PPy functionalized Fe_3O_4 are named as “epoxy/ Fe_3O_4 -PPy”. Epoxy nanocomposites with as-received Fe_3O_4 are named as “epoxy/ Fe_3O_4 ”. Epoxy nanocomposites with PPy are named as “epoxy/PPy” and the epoxy nanocomposites with a physical mixture of PPy and Fe_3O_4 are named as “epoxy/ Fe_3O_4 /PPy”. As shown in **Figure 6.1(B)**, the nanofillers were immersed in Epon 862 resin overnight to wet the nanoparticles. Then the suspension was mechanically stirred

for 1 hour (600 rpm, Heidolph, RZR 2041). After that, the curing agent of EpiCure W was added into the Epon resin nanosuspensions with a monomer/curing agent ratio of 100/26.5 for 1 hour mechanical stirring (200 rpm). Then the solution was mechanically stirred at 70 °C for 2 hours (200 rpm), which was essential to remove the bubbles and to prevent the sedimentation of the Fe₃O₄ nanoparticles during the curing process. Finally, the solutions were poured into the silicone molds and cured at 120 °C for 5 hours.

6.2.3 Characterization

The morphology of as-synthesized materials was examined by a FEI Helios NanoLab 600i scanning electron microscope (SEM, Hillsboro, OR). All the samples were sputter coated with a thin layer of carbon (about 3 nm) to ensure good imaging. The magnetic properties were investigated in a 9-Tesla Physical Properties Measurement System (PPMS) by quantum design at room temperature.

The volume resistivity was measured by testing the DC resistance along the disc samples with a diameter of about 60 mm with an Agilent 4339B high resistance meter. It allows us to the resistivity measurement up to $10^{16} \Omega \text{ cm}$. A four-probe technique (C4S 4-Point Probe Head Cascade Microtech, the probe tips were made of tungsten carbide) was used for the measurement.

Tensile test was carried out following ASTM, D412-98a in a unidirectional tensile test machine (ZQ-20B-1 tensile strength testing system). The samples (dog bone shaped) were designed according to the ASTM standard requirement and prepared as described for the epoxy nanocomposites in the molds. A crosshead speed of 0.26 mm/s was used and the

strain (mm mm^{-1}) was calculated by dividing the jogging displacement by the original gauge length.

The relative complex permeability ($\mu = \mu' + \mu''$) and permittivity ($\varepsilon = \varepsilon' + \varepsilon''$) were measured by a network analyzer (Agilent Technologies model N5232A) based on the transmission line technique, as shown in **Figure 6.1 (B)**. A donut shaped sample was cut from the as-prepared nanocomposites. The outer and inner diameters of the specimen were 7.00 and 3.04 mm, respectively. The specimen was then placed in a sample holder, which was located between the rigid beaded airline (APC-7) and the flexible coaxial airline (APC-7) that were connected to the network analyzer. The frequency of electromagnetic waves tested was ranged from 100 MHz to 20 GHz. The permeability and permittivity were directly read by the software.

Microscale combustion calorimetry (MCC) was utilized to evaluate the fire hazards by measuring combustion behaviors of the milligram-sized samples by a Govmark Microscale Combustion Calorimeter (Model MCC-2) operated at a heating rate of 1 °C/s in range from 90 to 650 °C in the pyrolysis zone. The samples were tested according to ASTM guidelines (ASTM D7309–07). Briefly, the combustion zone was set at 650 °C. The oxygen and nitrogen flow rates were set at 20 and 80 mL/min, respectively. The heat release rate (HRR) in watts per gram of sample (W/g) was calculated from the oxygen depletion measurements. The heat release capacity (HRC) in J/(g·K) was obtained by dividing the sum of peak HRR by the heating rate in K/s. The total heat release (THR) in kJ/g was obtained by integrating the HRR curve. The char yield was obtained by weighing the sample before and after the test.

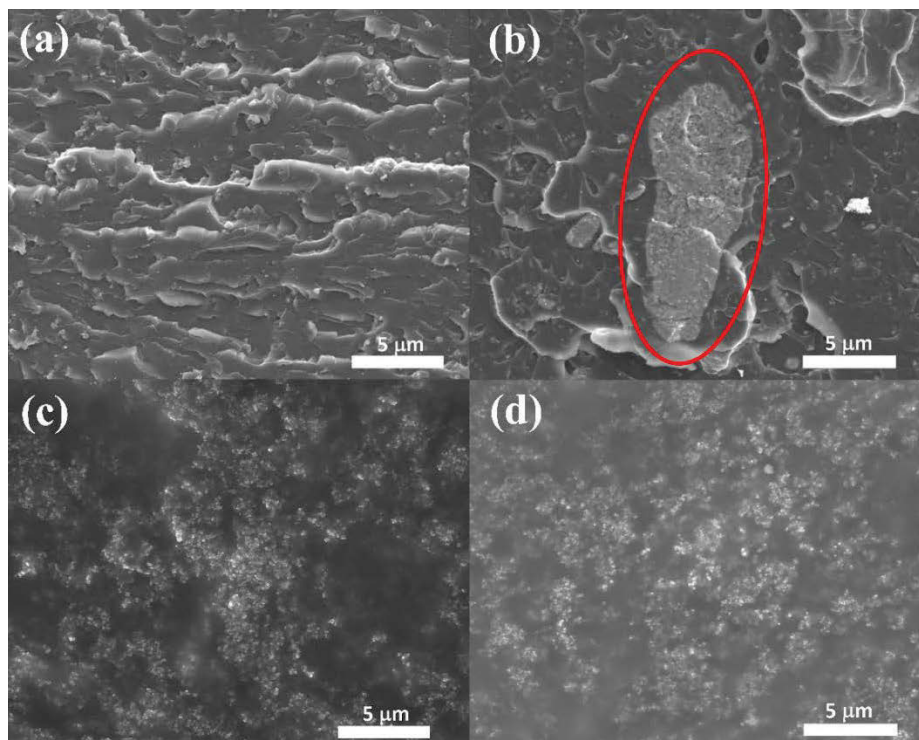


Figure 6.2 SEM image of (a) epoxy/(7.5 wt%)PPy, (b) epoxy/(30.0 wt%)Fe₃O₄ (red cycle indicating the agglomeration of Fe₃O₄), (c) epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, and (d) epoxy/(30.0 wt%) Fe₃O₄-PPy.

6.3 Results and discussions

6.3.1 SEM analysis

Figure 6.2 shows the dispersion quality of the nanoparticles in the epoxy matrix. The surface with “river-liked pattern” is observed in the SEM microstructure of epoxy/(7.5wt%)PPy, and the PPy nanoparticles are homogenously distributed in the epoxy matrix, **Figure 6.2(a)**. For the epoxy/(30.0wt%)Fe₃O₄, the agglomeration of the Fe₃O₄ is obviously observed, which is marked by red cycle in **Figure 6.2(b)**. Compared with epoxy/(7.5 wt%)PPy, the density of “river-liked” pattern appeared to be decreased in the SEM image of the epoxy/(30.0 wt%)Fe₃O₄. It indicates that the Fe₃O₄ nanoparticles prevent the formation of a brittle fracture since the load is transferred from the weaker epoxy matrix to the stronger Fe₃O₄ nanoparticles. a similar phenomenon is also observed in the epoxy nanocomposites with silica nanoparticles.³⁵ For the epoxy nanocomposites with the physically mixed PPy and Fe₃O₄ nanoparticles, **Figure 6.2(c)**, the “river like” patterns totally disappeared. The dispersion quality of the Fe₃O₄ nanoparticles in the epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy is much better than that of the epoxy/(30.0 wt%)Fe₃O₄, indicating that the PPy nanoparticles enhanced the dispersion quality of the Fe₃O₄ nanoparticles in the epoxy matrix. The epoxy nanocomposites with PPy functionalized Fe₃O₄, **Figure 6.2(d)**, show a relatively better dispersion quality than that of the epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, due to the interaction between the PPy on the functionalized Fe₃O₄ nanoparticles and the epoxy matrix.⁷

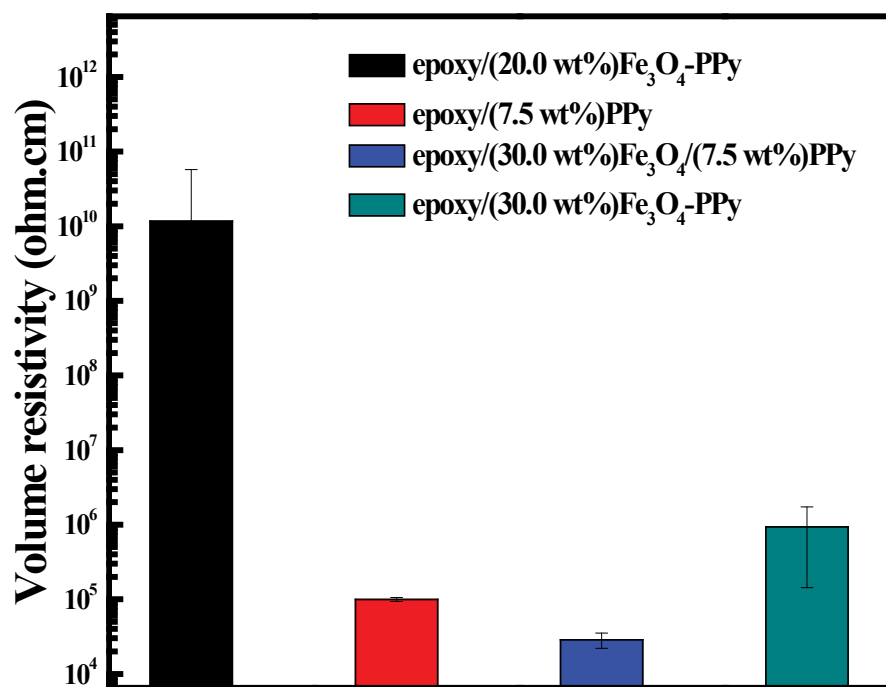


Figure 6.3 Volume resistivity of epoxy/(20.0 wt%)Fe₃O₄-PPy; epoxy/(7.5 wt%)PPy; epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy; epoxy/(30.0 wt%) Fe₃O₄-PPy.

6.3.2 Volume resistivity

Figure 6.3 shows the volume resistivity of epoxy nanocomposites with different nanofillers at room temperature. The volume resistivity of the epoxy/(20.0 wt%)Fe₃O₄-PPy is about 1.2×10^{10} ohm·cm, which is much higher than those of the epoxy/(7.5 wt%)PPy (about 9.9×10^4 ohm·cm), epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy (about 2.9×10^4 ohm·cm), and epoxy/(30.0 wt%)Fe₃O₄-PPy (about 9.3×10^5 ohm·cm). Even though the volume resistivity of the epoxy/(30.0 wt%)Fe₃O₄-PPy is a little higher than that of the epoxy/(7.5 wt%)PPy and the epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, the volume resistivity decreased 5 orders of magnitude compared with that of the epoxy/(20.0 wt%)Fe₃O₄-PPy nanocomposites, indicating that the electrical conductivity is transformed from insulating materials to semiconductor materials.³⁶⁻³⁸

6.3.3 Magnetic property

Figure 6.4 shows the magnetization curves of the epoxy/(30.0 wt%) Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, respectively. For all the samples, no hysteresis loop, *i.e.*, zero coercivity (H_c), is observed (see the right inset picture in **Figure 6.4**), indicating a superparamagnetic behavior of all the samples. The saturation magnetization (M_s) can be obtained by the extrapolated saturation magnetization from the intercept of $M - H^{-1}$ at high magnetic field.³⁹⁻⁴² The obtained M_s is 19.9, 15.9, and 16.0 emu/g for epoxy/(30.0 wt%)Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, respectively. Based on the M_s of 60.8 emu/g for the Fe₃O₄ nanoparticles in our previous report,⁷ the particle loading in the epoxy/(30.0 wt%)Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy is 32.7, 26.2, and

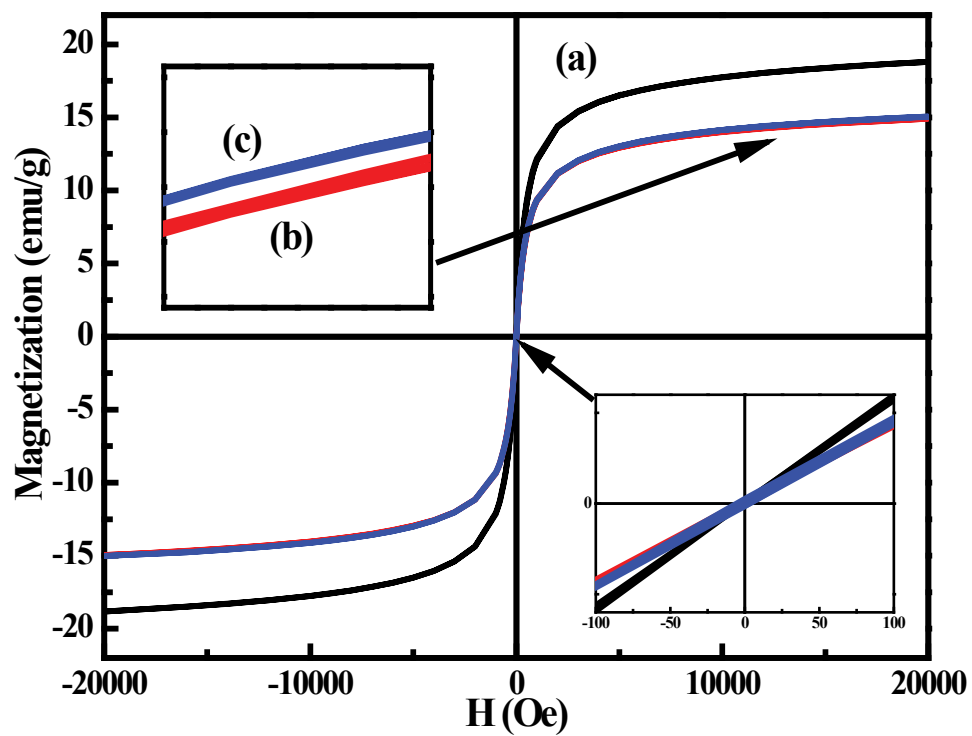


Figure 6.4 Room temperature magnetization as a function of magnetic field for (a) epoxy/(30.0 wt%) Fe_3O_4 -PPy, (b) epoxy/(30.0 wt%) Fe_3O_4 , and (c) epoxy/(30.0 wt%) Fe_3O_4 /(7.5 wt%) PPy, respectively.

26.3 wt%, respectively. It is consistent with our initial nanoparticle loading of 30.0 wt%. The same phenomenon was observed in the SiC–Fe₃O₄ hybrid nanowires.⁴³ For the superparamagnetic system, the magnetic property can be studied by the Langevin equation 1:²⁶

$$\frac{M}{M_s} = \coth(aH) - \frac{1}{(aH)} \quad (1)$$

where M is the magnetization (emu/g) of the materials under magnetic field (H , Oe), $a(T^{-1})$ is related to the electron spin magnetic moment m of the individual molecule as described in equation 2:

$$a = \frac{m}{k_B T} \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature. The parameter a calculated by the polymath software for epoxy/(30.0 wt%)Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy is 3.5, 3.3 and 3.3 T⁻¹, respectively. Based on equation 2, the values of m for epoxy/(30.0 wt%)Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy is 1.40, 1.32 and 1.32 μ_B , respectively. In our previous work, the m of the as-received Fe₃O₄ nanoparticles was found to be 1.19 μ_B .⁷ Therefore, the PPy and epoxy matrix have little effect on the magnetic moment of the Fe₃O₄ nanoparticles, no matter that the Fe₃O₄ nanoparticles are coated by PPy or physically mixed with PPy in the epoxy matrix.

6.3.4 Mechanical property

Figure 6.5 shows the tensile-stress curve of the cured epoxy nanocomposites. The tensile strength of epoxy/(7.5 wt%)PPy is 70.76 MPa ,which is much higher than the other

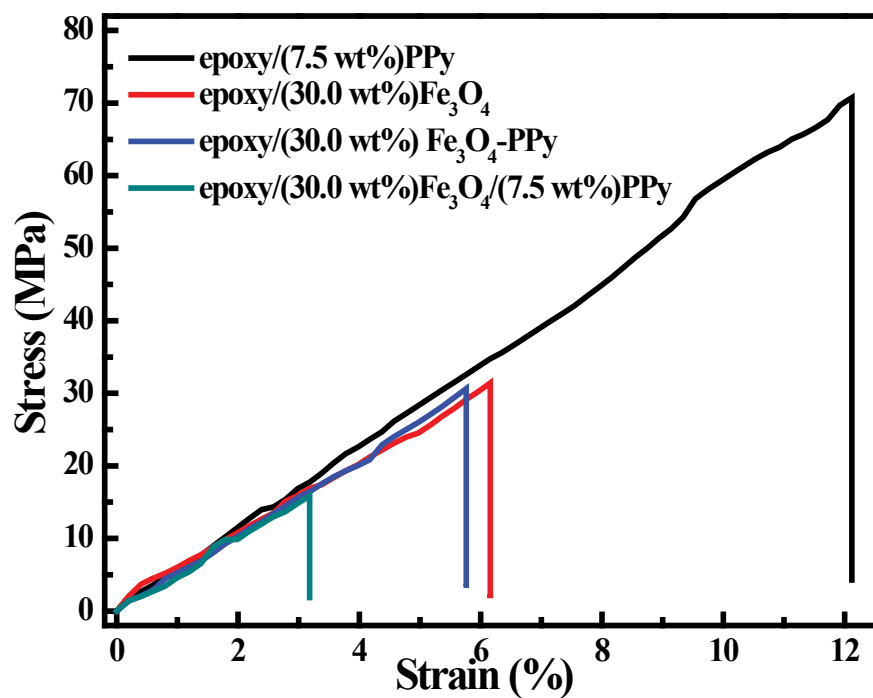


Figure 6.5 Stress–strain curves of epoxy/(7.5 wt%) PPy, epoxy/(30.0 wt%)Fe₃O₄, epoxy/(30.0 wt%) Fe₃O₄-PPy and epoxy/(30.0 wt%)Fe₃O₄/(7.5 wt%)PPy, respectively.

three magnetic epoxy nanocomposites in this work. The tensile strength of epoxy/(30.0 wt%) Fe_3O_4 is 31.45 MPa, which is the same as epoxy nanocomposites with PPy functionalized Fe_3O_4 (The tensile strength is 30.65 MPa). In the previous work, the conductive polymer could serve as a coupling agent between the epoxy matrix and nanoparticles which could enhance the mechanical property of the epoxy nanocomposites.^{7, 44} However, due to the high loading of Fe_3O_4 /PPy in the epoxy matrix, the epoxy/(30.0 wt%) Fe_3O_4 -PPy did not show enhanced mechanical property compared with epoxy/(30.0 wt%) Fe_3O_4 .⁷ And the tensile strength of epoxy/(30.0 wt%) Fe_3O_4 /(7.5 wt%)PPy is only 15.83 MPa which is lower than that of epoxy/(30.0 wt%) Fe_3O_4 , because except the 30.0 wt% Fe_3O_4 , 7.5 wt% PPy is also added into the epoxy. The Young's modulus is the slope of the stress–strain curve at elastic portion. The Young's modulus of epoxy/(30.0 wt%) Fe_3O_4 is larger than that of epoxy/(7.5 wt%)PPy; and epoxy/(30.0 wt%) Fe_3O_4 /(7.5 wt%)PPy shows larger Young's modulus than that of epoxy/(30.0 wt%) Fe_3O_4 -PPy. The variation in elongation-to-break shows opposite trend as compared to the change in Young's modulus.⁶ The toughness can be determined by integrating the stress–strain curve ($422.44 \text{ J}\cdot\text{m}^{-3}\cdot 10^4$ for epoxy/(7.5 wt%)PPy > $98.77 \text{ J}\cdot\text{m}^{-3}\cdot 10^4$ for epoxy/(30.0 wt%) Fe_3O_4 > $86.27 \text{ J}\cdot\text{m}^{-3}\cdot 10^4$ for epoxy/(30.0 wt%) Fe_3O_4 -PPy > $25.24 \text{ J}\cdot\text{m}^{-3}\cdot 10^4$ for epoxy/(30.0 wt%) Fe_3O_4 /(7.5 wt%)PPy). The Toughness shows the same trend as the elongation-to-break.

6.3.5 Microwave absorption performance

Figure 6.6 shows the frequency dependent real part (ϵ') and imaginary part (ϵ'') of the relative complex permittivity ($\epsilon_r = \epsilon' + i\epsilon''$); the ϵ' and ϵ'' stand for storage and loss

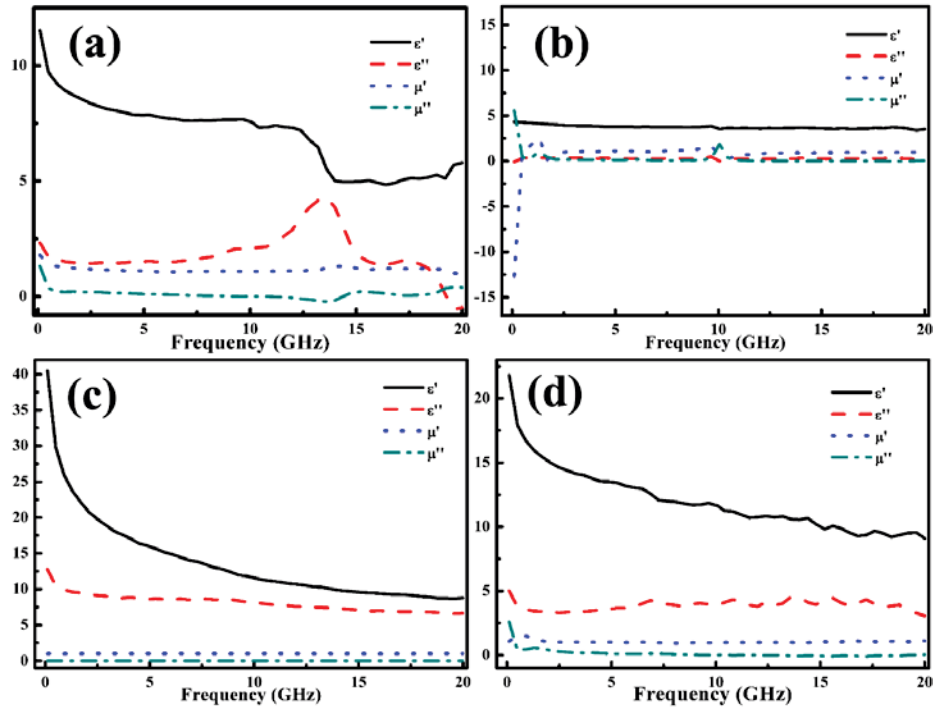


Figure 6.6 Permittivity and permeability vs frequency of (a) epoxy/(20.0 wt%) Fe_3O_4 -PPy, (b) epoxy/(30.0 wt%) Fe_3O_4 , (c) epoxy/(7.5 wt%) PPy, and (d) epoxy/(30.0 wt%) Fe_3O_4 -PPy.

capability of electric energy. And the frequency dependent real part (μ') and imaginary part (μ'') of the relative complex permeability ($\mu_r = \mu' + i\mu''$), the μ' and μ'' stand for the storage and loss capability of magnetic energy. The ε' for all the samples decreases with increasing the frequency. The ε' value decreases from 11 to 4 for epoxy/(20.0 wt%) Fe₃O₄-PPy in **Figure 6.6(a)**. The ε' value of epoxy/(30.0 wt%)Fe₃O₄ is almost constant in the measured frequency, **Figure 6.6(b)**. For epoxy/(7.5 wt%)PPy and epoxy/(30.0 wt%)Fe₃O₄-PPy, the ε' value decreases from 40 to 8 and from 22 to 9 in **Figure 6.6(c-d)**, respectively. An obvious peak at around 13 GHz is observed for the ε'' in the epoxy/(20.0 wt%)Fe₃O₄-PPy, **Figure 6.6(a)**, which is due to the resonance behavior of the Fe₃O₄ in the epoxy/(20.0 wt%)Fe₃O₄-PPy nanocomposites.⁴⁵ A similar phenomenon is also observed in the Co/C nanoparticles.⁴⁶ The ε'' of other three samples is almost constant within the measured frequency. And the ε'' value of epoxy/(7.5 wt%)PPy is larger than other three samples. According to the free electron theory, the σ (electrical conductivity) is related to ε'' and expressed by equation (3):^{46, 47}

$$\sigma = 2\pi\varepsilon_0\varepsilon''f \quad (3)$$

where ε_0 is the free space permittivity and f is the frequency. The ε'' of epoxy/(7.5 wt% PPy) is larger than those of the epoxy nanocomposites with as-received Fe₃O₄ and Fe₃O₄-PPy nanoparticles; therefore the epoxy/(7.5 wt% PPy) also shows a higher electrical conductivity, which is consistent with the result in the volume resistivity section. In **Figure 6.6(a)**, the μ' and μ'' values of epoxy/(20.0 wt%) Fe₃O₄-PPy are slightly changed within the measured frequency (μ' about from 1-1.7 and μ'' about from 0 to 1.3). For epoxy/(30.0 wt%)Fe₃O₄, the μ' and μ'' values are almost constant, however, the peaks are observed at

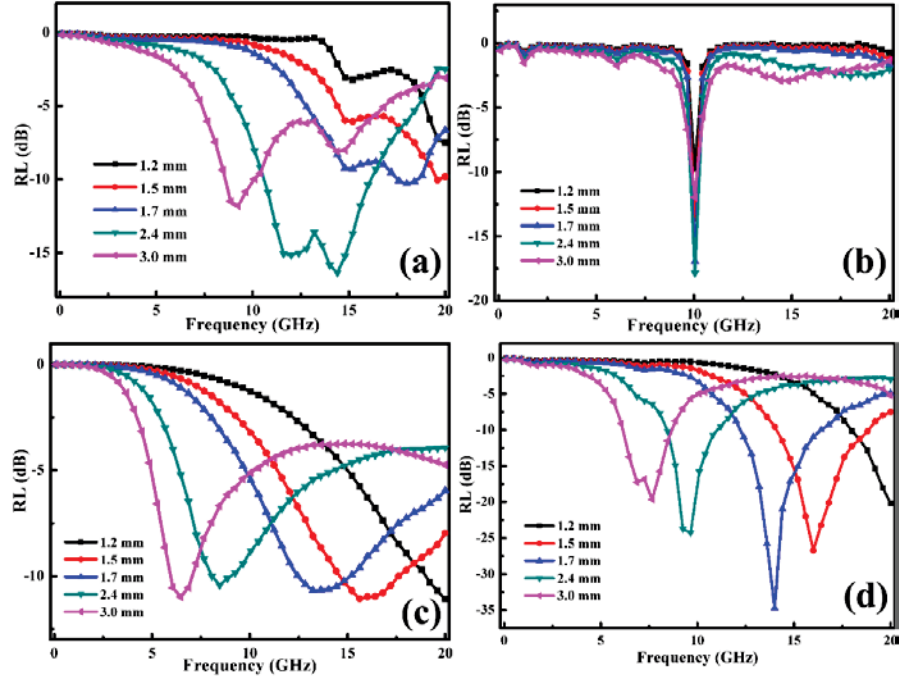


Figure 6.7 Dependence of RL on the thickness of the absorption layer within the frequency range of 0.1-20.0 GHz: (a) epoxy/(20.0 wt%) Fe₃O₄-PPy, (b) epoxy/(30.0 wt%) Fe₃O₄, (c) epoxy/(7.5 wt%) PPy and epoxy/(30.0 wt%) Fe₃O₄-PPy.

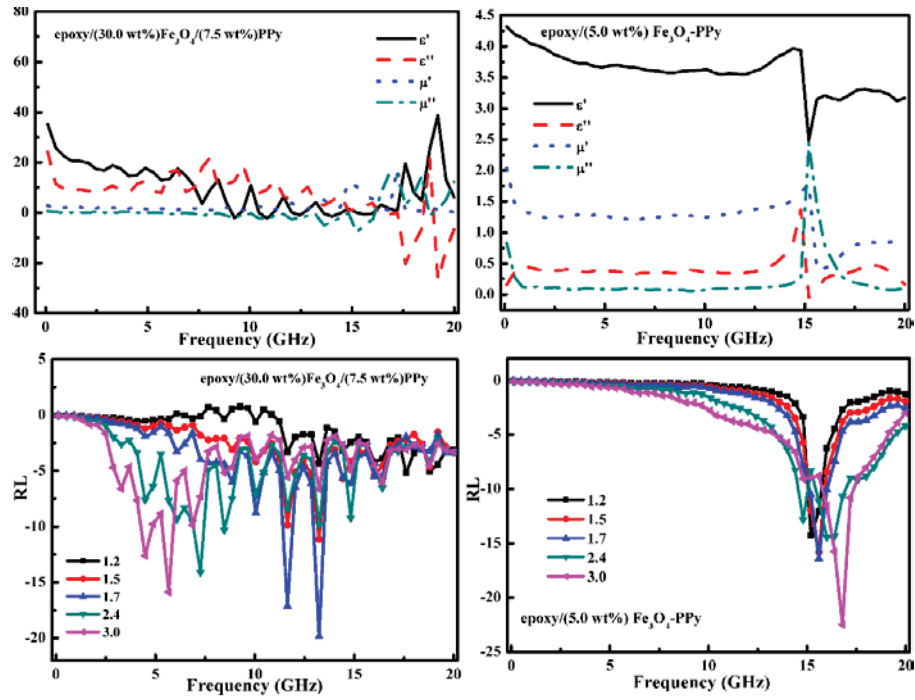


Figure 6.8 Permittivity and permeability vs frequency and dependence of RL on the thickness of the absorption layer within the frequency range of 0.1-20.0 GHz for epoxy nanocomposites.

Table 6.1 Microwave absorption properties of HRR as a function of temperature for epoxy/(20.0 wt%) Fe₃O₄-PPy, epoxy/(30.0 wt%)Fe₃O₄, epoxy/(7.5 wt%)PPy and epoxy/(30.0 wt%) Fe₃O₄-PPy.

Sample	Minimum RL value (dB)	Thickness (mm)	Absorption bandwidth (≤10 dB)	Absorption bandwidth (≤20 dB)
20.0 wt% Fe ₃ O ₄ -PPy	-16.4	2.4	5.9	0
30.0 wt% Fe ₃ O ₄	-17.8	2.4	0	0
7.5 wt% PPy	-11.0	1.5	1.2	0
30.0 wt% Fe ₃ O ₄ -PPy	-35.7	1.7	4	0.8

around 10 GHz in **Figure 6.6(b)**. The μ' is 1 and the μ'' is 0 in **Figure 6.6(c)** since there is no magnetic component in the epoxy/(7.5 wt%)PPy. In **Figure 6.6(d)**, the μ' is almost constant at 1, the μ'' slightly decreases from 0.6 to 0.

The reflection loss (RL) is calculated based on the transmission line theory to study the microwave absorption properties.⁸ The RL of the electromagnetic radiation under normal wave incidence on a single layer material surface backed by a perfect conductor can be defined by equation 4:^{5, 48}

$$RL = -20 \log_{10} \left| \frac{Z - 1}{Z + 1} \right| \quad (4)$$

where Z represents the input impedance at the interface of free space and tested materials.

The Z can be expressed as equation 5:⁵

$$Z = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left(-i \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right) \quad (5)$$

where μ_r and ε_r are the relative complex permeability and permittivity, respectively. The f is the frequency of the electromagnetic wave, d is the thickness of the tested material, and c is the velocity of electromagnetic waves in free space.⁴⁹ The RL of these epoxy samples with thickness varied from 1.2 to 3.0 mm is calculated and displayed in **Figure 6.7**. Generally, the RL below -10, -20 and -30 dB is 90.0, 99.0 and 99.9% attenuation of the incident electromagnetic wave, respectively. The electromagnetic wave absorption properties of these epoxy samples are summarized in **Table 6.1** In **Figure 6.7(a)**, the minimum RL of epoxy/(20.0 wt%)Fe₃O₄-PPy is -16.4 dB when the thickness is 2.4 mm, the absorption bandwidth below -10 dB is 5.9 GHz. However, the bandwidth below -20 dB is 0 GHz. For epoxy/(30.0 wt%)Fe₃O₄, **Figure 6.7(b)**, although the minimum RL value is

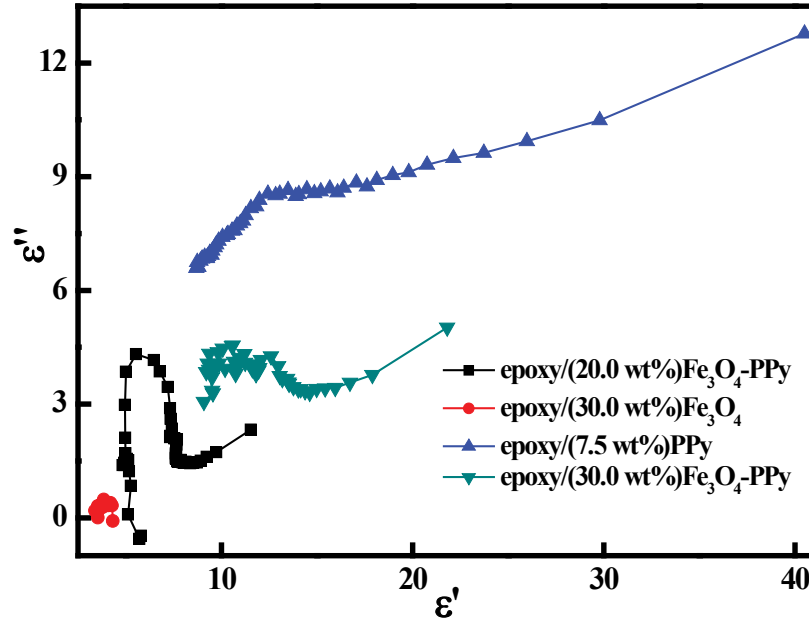


Figure 6.9 Frequency dependence of the Cole-Cole semicircles for the epoxy/(20.0 wt%) Fe_3O_4 -PPy, epoxy/(30.0 wt%) Fe_3O_4 , epoxy/(7.5 wt%) PPy and epoxy/(30.0 wt%) Fe_3O_4 -PPy.

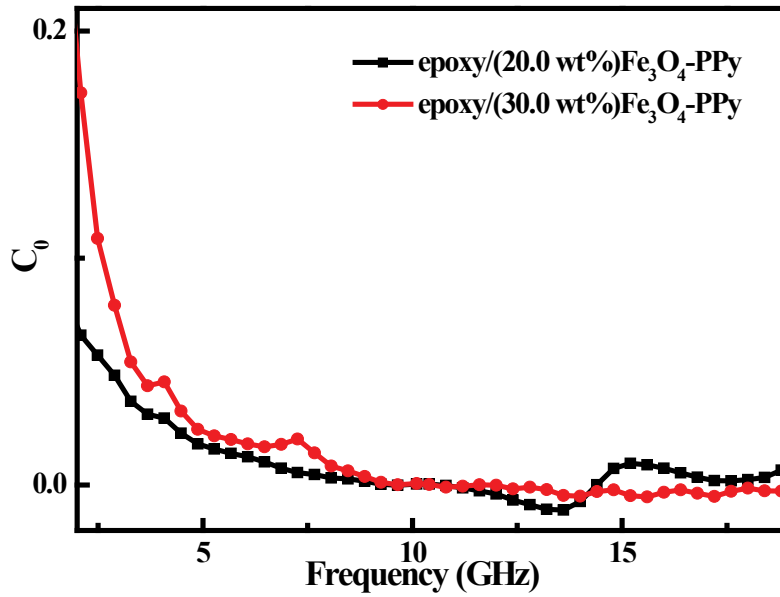


Figure 6.10 C_0 - f curves of epoxy/(20.0 wt%) Fe_3O_4 -PPy and epoxy/(30.0 wt%) Fe_3O_4 -PPy.

-17.8 dB, the absorption bandwidth below -10 dB is 0 GHz. For epoxy/(7.5 wt%) PPy, **Figure 6.7(c)**, the absorption bandwidth below -10 dB is only 1.2 GHz, and below -20 dB is 0 GHz. Even though the above three samples show electromagnetic wave absorption, the absorption bandwidth below -10 and -20 dB is not good enough for real EMI shielding application. Compared with the above three samples, the epoxy/(30.0 wt %)Fe₃O₄-PPy in **Figure 6.7(d)**, shows a much enhanced electromagnetic wave absorption property. The minimum RL value even reaches -35.7 dB, whereas the RL below -10 dB is 4 GHz and RL below -20 dB is 0.8 GHz. The RL of the epoxy/(30.0 wt %)Fe₃O₄/(7.5 wt%)PPy is shown in **Figure 6.8**, and the absorption bandwidth below -10 and -20 dB are almost 0 GHz. With the same loading of Fe₃O₄ nanoparticles and PPy, the electromagnetic wave absorption performance of epoxy with physical mixture of Fe₃O₄ and PPy is very poor, however, the epoxy with PPy coated Fe₃O₄ nanoparticles shows much enhanced electromagnetic wave absorption performance mainly because the PPy coated Fe₃O₄ nanoparticles make a better electromagnetic matching.⁵⁰

There are many factors that influence the electromagnetic absorption properties, such as dielectric loss, magnetic loss and characteristic impedance.⁵¹⁻⁵⁴ Based on equation (5), at the same thickness, if the dielectric loss contribution and magnetic loss contribution were well matched, the material would show an enhanced electromagnetic wave absorption property. The electromagnetic energy is transformed to joule thermal energy during the polarization process for the dielectric material, which results in the microwave attenuation. This could be described by the Debye relaxation using equation (6):⁴⁵

$$(\varepsilon' - \varepsilon_{\infty})^2 + (\varepsilon'')^2 = (\varepsilon_s - \varepsilon_{\infty})^2 \quad (6)$$

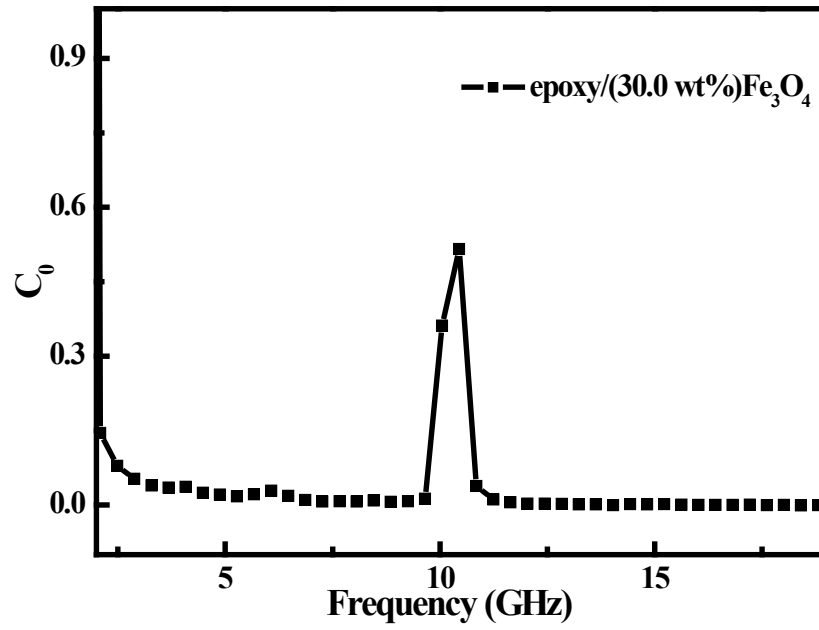


Figure 6.11 C_0 - f curves of epoxy/(30.0 wt%) Fe_3O_4 nanocomposite.

where ε_s is the static permittivity and ε_∞ is the relative dielectric permittivity at the high-frequency limit. The plot of ε'' vs. ε' would be semicircle, denoted as the Debye semicircle. Each semicircle corresponds to a Debye dipolar relaxation. **Figure 6.9** shows the ε' - ε'' curves of epoxy samples. It is obvious that the epoxy/(30.0wt%)Fe₃O₄ nanocomposites present a totally disordered curve with no semicircle and dielectric relaxation.⁴⁵ For epoxy/(20.0 wt%)/Fe₃O₄-PPy and epoxy/(30.0 wt%)/Fe₃O₄-PPy, there are two semicircles observed, which correspond to two dielectric relaxation processes. However, there is one semicircle observed in the epoxy/(7.5 wt%)PPy nanocomposites. From the above results, the PPy functionalized Fe₃O₄ epoxy nanocomposites enhanced the EMI shielding performance, because of the interface polarizations between Fe₃O₄ and PPy, and between PPy and epoxy matrix.⁷ However, there is only one interface polarization between PPy and epoxy and there is no magnetic loss in the epoxy/(7.5 wt%)PPy nanocomposites. Therefore, epoxy/(7.5 wt%)PPy nanocomposites show poor electromagnetic absorption property.

It is well known that the magnetic loss is mainly induced by the natural resonance, exchange resonance and eddy current loss.^{46, 54, 55} The magnetic loss is usually induced by the eddy current loss at high frequency region, which can be evaluated by equation 7:⁵

$$\mu'' = 2\pi\mu_0(\mu')^2\sigma d^2 f/3 \quad (7)$$

where σ (S/m) is the electrical conductivity and μ_0 (H/m) is the permeability in vacuum. In general, if the reflection loss is induced by the eddy current, the values of C_0 ($C_0 = \mu''(\mu')^{-2}f^{-1}$) are constant when the frequency is changing. It is obvious that the C_0 of epoxy with PPy functionalized Fe₃O₄ nanoparticles is constant at high frequency, **Figure 6.10**. Due to higher loading of Fe₃O₄-PPy nanoparticles in epoxy/(30.0 wt%)Fe₃O₄-PPy,

the C_0 of epoxy/(30.0 wt%)Fe₃O₄-PPy nanocomposites is relatively more constant than that of epoxy/(20.0 wt%)Fe₃O₄-PPy nanocomposites. For epoxy/(30.0 wt%)Fe₃O₄ in **Figure 6.11**, the C_0 is constant, however, the electromagnetic absorption ability is very poor. It indicates that the magnetic loss did not match well with dielectric loss and limited the electromagnetic absorption.⁴⁵

On the other hand, better magnetic absorption property is due to the enhanced anisotropic energy (H_a), a higher anisotropic energy and a better electromagnetic absorption properties as shown in equation 8:⁸

$$H_a = 4|K_1|/3\mu_0 M_s \quad (8)$$

where $|K_1|$ is the anisotropic coefficient. A higher anisotropic energy, a better electromagnetic absorption. The calculated M_s for epoxy/(20.0 wt%)Fe₃O₄-PPy, epoxy/(30.0 wt%) Fe₃O₄, epoxy/(30.0 wt%)Fe₃O₄/(7.5wt%)PPy, and epoxy/(30.0 wt%)Fe₃O₄-PPy are 13.1, 15.9, 16.0 and 19.9 emu/g, respectively.⁷ The H_a of epoxy/(20.0 wt%)Fe₃O₄-PPy is higher than H_a of the other three samples. The higher anisotropic energy is helpful to improve the electromagnetic wave absorption property.⁸ Therefore, epoxy/(20.0 wt%)Fe₃O₄-PPy shows better electromagnetic absorption properties than epoxy/(30.0 wt%) Fe₃O₄, and epoxy/(30.0 wt%)Fe₃O₄/(7.5wt%)PPy nanocomposites. However, even H_a of epoxy/(20.0 wt%)Fe₃O₄-PPy is higher than that of epoxy/(30.0 wt%)Fe₃O₄-PPy, the electromagnetic wave absorption property of epoxy/(30.0 wt%)Fe₃O₄-PPy is much better, indicating there are other effects (such as dielectric loss and magnetic loss) on the electromagnetic absorption property. In other word, the epoxy

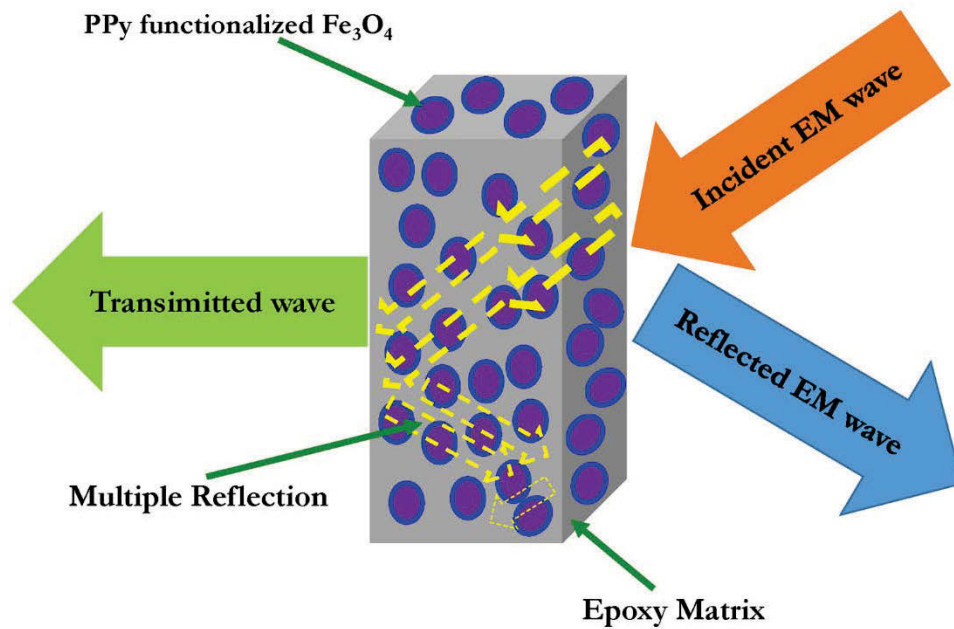


Figure 6.12 Schematic illustrations of the EMI shielding performance of epoxy/ Fe_3O_4 -PPy nanocomposites.

nanocomposites with PPy functionalized Fe_3O_4 show enhanced electromagnetic absorption property due to the increased interface area formed between PPy and Fe_3O_4 and the fact that the magnetic loss well matches dielectric loss. The eddy current loss, enhanced anisotropic energy and interface polarization have all contributed to the enhanced electromagnetic wave absorption of epoxy/ Fe_3O_4 -PPy nanocomposites. The proposed EMI shielding mechanism is showed in **Figure 6.12**. The EM wave is attenuated by the nanocomposites, the attenuation of an EM wave includes absorption, reflection, and multiple reflections.^{56, 57} when a higher amount of Fe_3O_4 -PPy nanoparticles is loaded, a better electromagnetic absorption is achieved.

6.3.6 Combustion behavior and fire hazard

Figure 6.13 shows the HRR as a function of temperature for pure epoxy and epoxy/(30.0 wt%) Fe_3O_4 -PPy nanocomposites. **Table 6.2** shows the related heat release parameters. The HRR is one single important parameter to estimate the fire hazard of the flammable materials.⁵⁸ During fires, the materials with higher HRR would generate a heat flux, which is very dangerous. Therefore, it is important to decrease the HRR. For pure epoxy, the peak HRR is 470.3 w/g at 397.4 °C, the HR capacity and total HR are 453.0 J/g-k and 25.5 kJ/g, respectively. The HRR of pure epoxy is much lower than the thermoplastic materials polypropylene with HRR of 1513.0 w/g.⁵ The initial thermal decomposition temperature of epoxy/(30.0 wt%) Fe_3O_4 -PPy nanocomposites is lower than that of pure epoxy, which is consistent with the thermal stability property.⁷ Compared with pure epoxy, the peak HRR at 386.5 °C of epoxy/(30.0 wt%) Fe_3O_4 -PPy nanocomposite decreased to 292 w/g. And the HRR reduction of epoxy/(30.0 wt%) Fe_3O_4 -PPy is 36.4%. Apparently, the

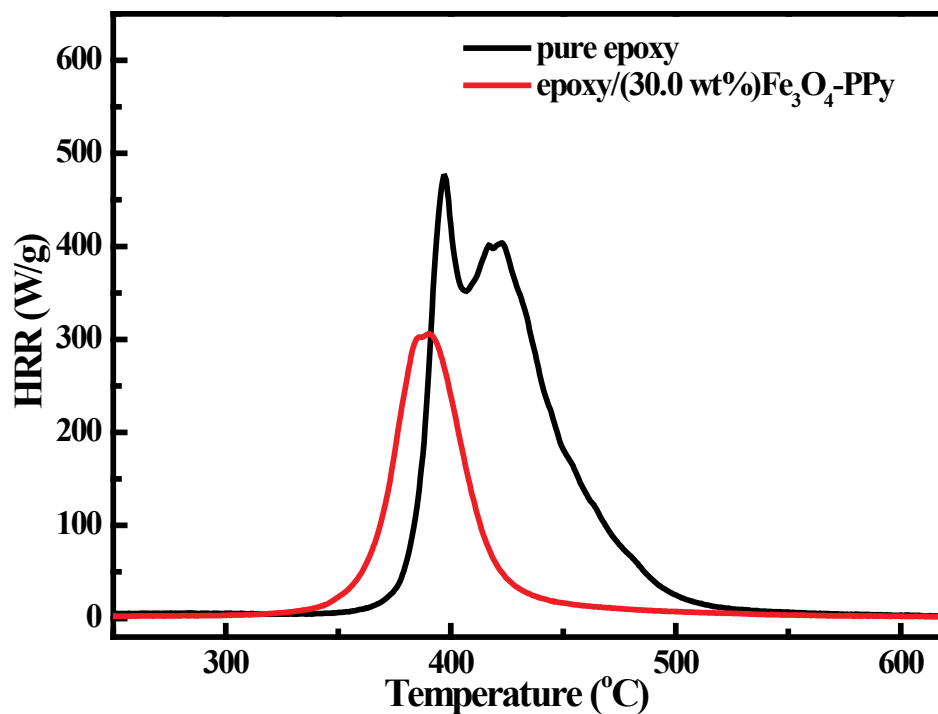


Figure 6.13 HRR as a function of temperature for pure epoxy and epoxy/(30.0 wt%) Fe₃O₄-PPy.

Table 6.2 Heat release parameters of pure epoxy and epoxy/(30.0 wt%) Fe₃O₄-PPy.

Sample	PHRR (W/g)	PHRR Reduction (%)	THR (kJ/g)	HR capacity (J/g-k)	Char (%)
Pure epoxy	470.3	---	25.5	453.0	6.2
Epoxy/(30.0 wt%) Fe ₃ O ₄ - PPy	299.2	36.4	12.3	292.0	49.2

reduced peak HRR is due to the dilution of pure epoxy after adding the nanoparticles. In our previous work, there is covalent bonding formed between PPy on the surface of Fe₃O₄ and epoxy matrix.⁷ The formed covalent bonding can postpone the degradation of the materials. A similar phenomenon was also observed in the polyaniline epoxy nanocomposites and other polymers.⁵⁹⁻⁶² The char residue of epoxy/(30.0 wt%)Fe₃O₄-PPy nanocomposites (49.2%) is much higher than that of pure epoxy (6.2%). The char yield is considered as characteristic of flame retardancy.^{34, 63} The formed char layer on the surface of the materials would keep the heat transferred from the heat source to the inner material and obstruct the distribution of combustible gases produced from the materials during the test as well.^{60, 64, 65} On the other hand, the epoxy/(30.0 wt%)Fe₃O₄-PPy nanocomposites contain PPy as well as the nitrogen element. Normally, the nitrogen-containing compounds are gas sources, this kind material can produce incombustible gases without toxic smoke during the degradation at high temperature.^{35, 60} The produced gas can dilute the concentration of oxygen near the flame.⁶⁶ Therefore, the epoxy/(30.0 wt%)Fe₃O₄-PPy nanocomposites show a decreased HRR and enhanced flame retardancy.

6.4 Conclusion

The epoxy nanocomposites reinforced with PPy functionalized Fe₃O₄ nanoparticles prepared by the SIP method show enhanced electromagnetic wave absorption performance. The magnetoresistance behavior was observed in PPy coated magnetic nanoparticles; thus, these magnetic epoxy nanocomposites has the potential for other applications such as magnetic sensor and information storage.^{26, 67} The epoxy/(30.0 wt%)Fe₃O₄-PPy nanocomposites with a thickness of 1.7 mm show good electromagnetic wave absorption

performance (the absorption bandwidth $RL < -10$ dB is 4.0 GHz and the absorption bandwidth $RL < -20$ dB is 0.8 GHz) with a minimum RL value of -35.7 dB. The enhanced electromagnetic wave absorption performance indicates the dielectric loss better match with magnetic loss, compared with epoxy with pure PPy or as-received Fe_3O_4 nanoparticles. The increased interface area, eddy current loss and increased anisotropy energy contribute to the improved electromagnetic wave absorption performance. According to the requirements of the Federal Communications Commission, our materials failed to meet the requirement for the common housing electronic equipment ($RL < -40$ dB),^{68, 69} however, if the particle loading is further increased, we believed that our epoxy nanocomposites have the potential to reach the requirement. Meanwhile, the combusted amount of the epoxy nanocomposites is almost half of the combusted amount of pure epoxy, which meets the requirement of the National Institute of Standards and Technology.⁷⁰ Therefore, the significantly reduced flammability make these nanocomposites suitable for safer electromagnetic wave absorber to satisfy stringent industrial standards. In other word, upon addition of the nanoparticles, the epoxy nanocomposites will have broader applications such as in aeronautics and aerospace industry, as anti-corrosion coatings and high voltage application.²¹

6.5 Reference

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Chapter 7. Conclusions

In this work, the applications of conductive polymer nanocomposites for magnetoresistance (MR) and electromagnetic shielding were reported, and the enhanced mechanical and electrical properties of epoxy nanocomposites with low loading polyaniline (PANI) nanoparticles were studied as well.

The PANI nanocomposites with different nanofillers including carbon nanomaterials (carbon black, carbon nanotube, carbon nanofiber and graphene), magnetic nanoparticles (Fe_3O_4 , Fe@C and CoFe_2O_4) and non-magnetic nanoparticles were synthesized by the surface initiated polymerization (SIP) method. The characteristic analysis of Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectra indicated that the PANI was successfully coated on the surface of the nanoparticles. The resistivity of all the PANI nanocomposites decreased with increasing the temperature, indicating a typical behavior of semiconductor. The quasi 3-d electron conduction mechanism was observed in all the PANI nanocomposites through the Mott variable range hopping (VRH) model. The nanofillers did not affect the charge transport mechanism of the PANI nanocomposites. The PANI nanocomposites with carbon nanomaterials or magnetic nanoparticles showed positive MR, while the TiO_2/PANI nanocomposites showed negative MR. Therefore, the MR values of the PANI nanocomposites can be controlled by the nanofillers. The wave functional shrinkage model and orbital magnetoconductivity theory (forward interference model) were applied to study the MR of the PANI nanocomposites. The localization length and average hopping length of the PANI nanocomposites decreased with increasing the magnetic field, and the density

of state at fermi level increased with increasing the magnetic field. In addition, the thermal stability and dielectric properties of the PANI nanocomposites were enhanced compared with pure PANI.

The epoxy nanocomposites with low loading of PANI nanoparticles were prepared by three different techniques. The PANI nanoparticles were synthesized by the oxidation polymerization method. The fabrication procedure can affect the dispersion quality of PANI nanoparticles in the epoxy matrix. Compared with pure epoxy, the PANI epoxy nanocomposites showed enhanced mechanical and electrical properties. When the PANI nanoparticle loading was 8.0 wt%, the volume resistivity of PANI epoxy nanocomposites decreased further, but the tensile strength of PANI epoxy nanocomposites was lower than that of pure epoxy which is due to the agglomeration of the PANI nanoparticles in the epoxy matrix. At the same PANI nanoparticle loading, the mechanical and electrical properties of PANI epoxy nanocomposites were affected by the synthesize method. Compared with pure epoxy, the PANI epoxy nanocomposites showed enhanced Young's modulus, but decreased toughness.

The epoxy nanocomposites reinforced with polypyrrole (PPy) functionalized Fe_3O_4 nanoparticles prepared by the SIP method showed enhanced electromagnetic wave absorption performance. The MR behavior was observed in PPy coated Fe_3O_4 nanoparticles, thus this magnetic epoxy nanocomposites have the potential for other applications such as magnetic sensor and information storage. The enhanced electromagnetic wave absorption performance indicates the dielectric loss better match with magnetic loss, compared with epoxy with pure PPy or as-received Fe_3O_4

nanoparticles. The increased interface area, eddy current loss and increased anisotropy energy contribute to the improved electromagnetic wave absorption performance. According to the requirements of the Federal Communications Commission, our materials did not meet the requirement for the common housing electronic equipment ($RL < -40$ dB), however, if the particle loading was further increased, we believed that our epoxy nanocomposites could reach that requirement. Meanwhile, with regard to the production of combustion products, the combusted amount of the epoxy nanocomposites is almost half of the combusted amount of the pure epoxy, which meets the requirement of the National Institute of Standards and Technology. Therefore, the significantly reduced flammability make these nanocomposites suitable for safer electromagnetic wave absorber to satisfy stringent industrial standards. In other word, upon addition of the nanoparticles, the epoxy nanocomposites will have broader applications such as in aeronautics and aerospace industry, as anti-corrosion coatings and high voltage application.

In summary, the MR behavior of PANI nanocomposites can be controlled by the nanofillers. The wave functional shrinkage model and orbital magnetoconductivity theory (forward interference model) described the effects of magnetic field, nanofillers and loading on the localization length, density of state at fermi level and average hopping length of the PANI nanocomposites. The fundamental study provided the information for the design of the conductive polymer based device. The epoxy nanocomposites with PPy coated Fe_3O_4 showed enhanced electromagnetic adsorption property and thermal stability.

In the future work, we will study the effects of magnetic field direction and temperature on the MR behavior of PANI nanocomposites. For the electromagnetic wave

shielding, we will study the effect of temperature on the electromagnetic shielding performance of conductive polymer nanocomposites, and the thermal conductivity of the polymer nanocomposites.

Vita

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