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UTILIZATION OF MULTIWALLED CARBON NANOTUBE /POLY(*p*-PHENYLENE) COMPOSITE FOR GAS DETECTION

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering Program in Chemical Engineering
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ปัญหาในด้านสภาวะแวดล้อมโดยเฉพาะมลภาวะทางอากาศเป็นปัญหาสำคัญอย่างหนึ่งในการใช้ชีวิตในปัจจุบัน ตัวรับรู้ที่มีความสามารถในการตรวจจับก๊าซพิษจึงมีความสำคัญเป็นอย่างมาก โดยในงานวิจัยนี้ได้มุ่งเน้นที่จะพัฒนาตัวรับรู้โดยใช้สารประกอบแต่งระหว่างท่อคาร์บอนระดับนาโนเมตรซึ่งมีคุณสมบัติเฉพาะทางไฟฟ้ากับพอลิเมอร์และสารประกอบโลหะออกไซด์

พอลิพีฟีนิลีน (Poly(p-phenylene)) ซึ่งเป็นพอลิเมอร์ที่มีความสามารถในการนำไฟฟ้า เนื่องจากมีพันธะคู่อยู่ในโมเลกุล ในงานวิจัยนี้ได้ทำการสังเคราะห์พอลิพีฟีนิลีนและสารประกอบโลหะออกไซด์ และได้ทำการวิเคราะห์โดยเครื่องมือวิเคราะห์ FTIR TGA SEM SPM และ XRD โดยศึกษาผลของระยะเวลาในการโซนิเคชัน ปริมาณของตัวทำละลาย ความเข้มข้นของก๊าซ และชนิดของก๊าซ ต่อคุณสมบัติของตัวเซนเซอร์

ท่อนาโนคาร์บอนซึ่งมีขนาดประมาณ 20 นาโนเมตร ถูกผสมกับพอลีพีฟีนิลีนโดยมีเทอพินอล (terpineol) เป็นตัวทำละลาย ศึกษาระยะเวลาที่ใช้ในการโซนิเคชันเพื่อที่จะหาสภาวะที่เหมาะสมในการเตรียมสารประกอบแต่งที่มีการกระจายตัวของท่อนาโนคาร์บอนที่ดี ในการทดลองพลังงานที่ใช้ในการโซนิเคชันเท่ากับ 750 วัตต์ ระยะเวลาที่ใช้ในการโซนิเคชันคือ 3 10 20 และ 30 นาที ซึ่งจากการทดลองพบว่าที่ระยะเวลา 10 นาทีเป็นระยะเวลาที่เหมาะสม นอกจากนี้ยังได้ทำการศึกษาผลของอัตราส่วนของสารต่างๆกับตัวทำละลายด้วย จากนั้นสารประกอบแต่งที่ได้ไปวัดอัตราการตอบสนองในทุกๆวินาที จากผลการทดลองพบว่าสารประกอบแต่งระหว่างท่อนาโนคาร์บอน พอลิพีฟีนิลีนและทังสเตนออกไซด์สามารถนำมาทำเป็นตัวเซนเซอร์ได้ โดยที่ท่อนาโนคาร์บอนจะให้ค่าการตอบสนอง (sensitivity) มากกว่า 40% ในขณะที่สารประกอบแต่งระหว่างท่อนาโนคาร์บอนกับทังสเตนออกไซด์ได้ค่าการตอบสนอง 11-15% และสารประกอบแต่งของท่อนาโนคาร์บอน พอลิพีฟีนิลีน และทังสเตนออกไซด์ให้ค่าการตอบสนอง 12-30%

ภาควิชา.......................วิศวกรรมเคมี.............................. ลายมือชื่อนิสิต..
สาขาวิชา.......................วิศวกรรมเคมี.............................. ลายมือชื่ออาจารย์ที่ปรึกษา..
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One of problems emerging in modern live is how to detect the existence of a gas in a room or space. The detection could be achieved by a sensor. The motivation of this work is to develop a sensor material consists of multiwalled carbon nanotubes (MWNTs), polymers, and metal oxides. Recently the combination of CNTs and polymer or metal oxides gains serious attention since the CNTs have unique electrical properties.

Poly(p-phenylene) (PPP) is known as a potential conductive polymer due to the existence of double bond. Based on information in published reports, the synthesizing of the PPP and the metal oxide successfully conducted. To observe comprehensively of materials synthesized, several characterizations were conducted such as FTIR, TGA, SEM, SPM, XRD. The materials then combined using a method to get a kind of composite as a sensor material. Several variables such as sonication time, amount of dispersant, types of gas, and gas concentration were varied to investigate the performance of the composite.

A certain ratio of MWNTs with nominal size of 20 nm and synthesized-PPP was compounded with the presence of terpineol as a dispersant. To investigate an optimal condition for homogenizing all constituents, ultrasonication with 750 watts was employed with compounding time of 3, 10, 20, 30 min. It was found that the composite film could be prepared with ultrasonication within 10 minutes. The ratio of constituents and the dispersant was also conducted. The composite was put into a system of sensing by which the response of the sensor material recorded automatically every second. A very important conclusion of this study is that the combination of MWNTs and PPP and tungsten oxide could be used as a sensor material. Typical results show that sensitivity of MWNTs was more than 40%,11-15% for MWNT/WO_3, and 12-30% for MWNT/PPP/ WO_3.

Department ..:.....Chemical Engineering..... Student's signature...................
Field of study..:...Chemical Engineering.... Advisor's signature...................
Academic year..: ...2009............................ Co-advisor's signature Mana Sriyudthsak

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CHAPTER I

INTRODUCTION

In this chapter academic background, motivations, objectives and the benefits of this research are deliberated.

1.1 Academic Background

From time to time in human life, technology has been continuously developed. Likewise the technology, the needs of human are unavoidable changed. Among various issues the need to get the materials which could increase the standard of our daily life should be intended by many researchers.

The last decade of the last century in condensed matter physics has been marked by the presence of carbon-based materials. The development of optical instrumentations has lead scientists to work with very-very small materials. Using the high-advanced of instrumentation scientists around the world can analyze, characterize, or measure the materials which popular called nanomaterials. Today, nanotechnology is a term addressed to system which handling such small materials. This technology has borderless hit in many fields and disciplines. Not only electronic but also medical and agricultural have been involved by nanotechnology (Miller and Senjen, 2008).

One of interesting and useful nanomaterials which was discovered at the end of 20th century is carbon nanotubes (CNTs). In 1991, Sumio Iijima at NEC reported that he found a new kind of carbon allotrope. His report in Nature spurs scientists to investigate means to synthesize and utilize the CNTs. Therefore up to now, besides the conventional forms of carbon, the graphite and the diamond, new forms of carbon which are fullerenes and carbon nanotubes has been recognized as promising materials which could provide various applications.

It has been accepted that, carbon nanotubes are driving significantly scientific research. At the beginning, the topic area was synthesis of CNTs. However, nowadays, interest includes the applications. Several important directions in basic research are continuously moves such as in chemistry, electronic transport, mechanicals, and field emission properties. Furthermore, the perspectives for applications are very challenging and exciting. As reported by Baughman et al. (2002) the main avenues of potential applications of carbon nanotubes are: electrochemical devices, hydrogen storage, field emission devices, sensor and probe.

How seriously scientists in research of nanomaterials could be described by amounts of paper published. Since 1991 to 2001 the papers related to CNTs are going increase (Baughman et al., 2002). In 2004 it is reported by Hennrich et al., (2005) that papers regarded to CNTs reached 5,000.

Regarding to achievements in nanotechnology, especially CNTs, could be described as reported that researchers at the Bhabha Atomic Research Center in India have been investigating the hollow carbon fibers as a potential water filter. They believe the unique chemical properties of nanotubes that only water molecules can pass through their interiors, while toxic metal ions, viruses, and bacteria cannot. The Indian research team has been trying to engineer nanoscale structures to form arrangements that can efficiently decontaminate water (Schwartz, 2008). Whereas, Sciendaily reported that a team at Purdue University has created a tiniest laser. The laser called *spaser* which work based on "nanophotonic" circuitry. Within the *spaser* there are spheres 44 nanometers in diameter. The *spaser* contains a gold core surrounded by a glasslike shell filled with green dye. When a light was shined on the spheres, plasmons generated by the gold core were amplified by the dye. The plasmons were then converted to photons of visible light, which was emitted as a laser. This innovation is paving the way for a host of innovations, including superfast computers that use light instead of electrons to process information, advanced sensors and imaging (Venere, 2009).

1.2 Why Do We Need Sensors

Basically, a sensor is a part of a controlling system which plays an important role in many situations and purposes. In modern era many places are equipped by sensor such as vehicles, cars, factories, planes, trains, and so on. Even in offices, houses, or shops the specific of sensor are available. Through the sensor, human be able to get information immediately regarding the specific condition at a moment. It can be said that sensor make our live more comfortable. For example, when in a room there is an unwanted smoke or gas emerging from a fire or other source, the sensor can give warning to people at that room so that many live might be saved using the sensor. Hence the existence of sensors has become a supporting need for our live.

To use a sensor one has to know in what condition he or she need the sensor. There is no a sensor can work for all condition. Therefore someone has to recognize types of sensor such as chemical sensors, biological sensors, gas sensors, physical sensors and so on. Recently, to take benefits from advanced technology scientists race to make sensors utilizing nanomaterials.

1.3 Brief Review on Sensor Development

Tremendous properties of CNTs have been appreciated by all scientists. Due to its electrical property, some scientists forecast in the future that the CNTs can shift the silicone which currently used in electronic (Collins and Avouris, 2000). In recent years, interest has grown in the development of an electronic "nose," capable of detecting mixed gases and even odors. The device can be used to environmental monitoring or other needs.

There are many aspects enable one to study sensor. As discussed by White (Muller et al., 1991) that the field of sensor could be divided into three categories such as technological aspect, sensor material, and field application. Each category has several topics which related to sensor performance. Some typically aspects listed in Table 1.1, of course, it is impossible to investigate all the aspects. Practically, the discussion about an aspect must be related to other aspects. Investigating of sensor materials leads to the question how sensitive the materials to its target. Then the requirement of sensitivity depend on what field the sensor will be applied.

A gas sensor is a structure, which consists of a substrate, an insulating layer, a sensor film and contacts. Each element of the structure may contribute into the conductivity process and influence gas sensor parameters (Ryabova, 2009). In advanced system the structure of sensor may be supported by other part such as heater which enables the sensor works at high temperature.

Table 1. 1 Several aspects for sensor study.

Technological Aspect	Sensor Material	Field Application
Sensitivity	Organic	Agriculture
Measuring range	Conductor	Automotive
Stability	Insulator	Civil engineering,
Resolution	Semiconductor	Construction
Selectivity	Biological substance	Energy medicine
Speed of response	Other (specify)	Information,
Ambient condition		Telecommunications
Output format		Marine
		Military
		Scientific measurement
		(excluding automotive)
		Other (specify)

1.4 Motivations of this Research

The CNTs has been a focus at least by material scientists. However, all aspects around the material have destroyed the border interdisciplinary. No one can claim that the study of CNTs belongs to his or her discipline. Therefore, researchers from different field can share their experiences for construction the knowledge of CNTs to lead improving human live quality. It is unsurprising that physical researchers could collaborate with their colleagues in medicals or electrical researchers get involved in a team with chemical engineers to investigate aspects of CNTs.

The synthesizing of CNTs currently is not so difficult. Although using simple methods some of member of Center of Excellence in Particle Technology (CEPT) successfully synthesized the material. The achievements of member of CEPT, in fact, should be developed to take its benefit. One idea to continue the work is to find the application of CNTs produced. In advanced thinking, the combination of knowledge in carbon nanotubes and polymers might be challenging in the future. Besides, many potential can be taken from study of both carbon nanotubes and polymers. In fact, this country has many sources of carbon such wood, gasoline, coal, and so on. In other side, polymers are alternative materials to get light material which has relatively good conductivity or high tensile strength. The materials of conductive polymer would be applied in airplanes or vehicles to reduce the production cost.

A simple way to combine the knowledge of polymer and CNTs could be achieved through fabricating a sensor material which consists of the two materials. In other word, a kind of polymers is mixed with CNTs to get a composite. Then the composite is exposed to an environmental where some gases or vapors are dispersed. The changing of composite will be analyzed using a measurement system.

1.5 Objectives of this Work

The most important from this work is getting ability to make a sensor material with multiwalled carbon nanotubes (MWNTs) and poly(*p*-phenylene) (PPP) as material-based. Until now the using of PPP as a sensor material has not thoroughly been reported yet. The applying of PPP could be a pioneer to next work.

The fabrication of a sensor material was conducted in a simple way. After fabrication of the sensor material, the next step was to test it by exposing it to chemical vapors. The developed sensors were exposed to various chemicals. Two aspects related to the sensitivity of sensor were gas concentration and types of gas. Those aspects were relevant to our experience in CEPT. Actually another factor which is worth to investigate is temperature. The limitations in sensing measurement, however, were an obstacle to work with elevated temperature.

1.6 The Benefits in this Research

During accomplishing this work several worthy benefits would be taken. Generally at least two benefits would be provided. First of all is getting communication network with supporting-research such as accesses to other laboratory out side of Department of Chemical Engineering. The sensor topic is very related to electrical field hence the accomplishing of works needs collaboration with a laboratory at Department of Electrical Engineering. Second is getting experiences and knowledge in field of carbon, polymer, characterization using SEM, FTIR, multimeter etc.

This research could be seen as a trigger to other similar project in the future. The weaknesses of work during accomplishing the experimental works should be improved. Therefore the better quality of sensor study might be achieved. It is hoped that papers concerning sensor study produced by CEPT of Chulalongkorn University would be more published in international journals.

CHAPTER II

FUNDAMENTALS AND LITERATURE REVIEW

In this chapter fundamentals and literature review of materials for sensor development is presented. It is employed as reference for further investigation in this work.

2.1 Carbon in General

Carbon is one of elements occupying almost of the earth. Human, plants and animals consist of plenty of carbon. Human being as well as animal can fulfill their needs using the carbon. Plants consisting of a lot of carbon ate by human and animal to do their activities. Besides, other human's needs got from carbon compound. Crude oil lifted from deep earth has been using to get chemicals with carbon basis.

Carbon heads the list of Group-IVA elements. Carbon has three well-known allotropic forms: diamond, graphite, and carbyne. It is known that carbon can exists in three valence states which correspond to sp^3, sp^2, and sp-hybridization of atomic orbital. In least decades there is a new kind of carbon called carbon nanotubes (CNTs). Before CNTs there was another form which called buckminsterfullerene or popularly called by buckyball i.e. C_{60}. Fig. 2.1 (Rao et al., 1995) presents the comparison of carbon allotropes. The respective structural motifs, the chair form of cyclohexane and the benzene ring are shown with thick lines.

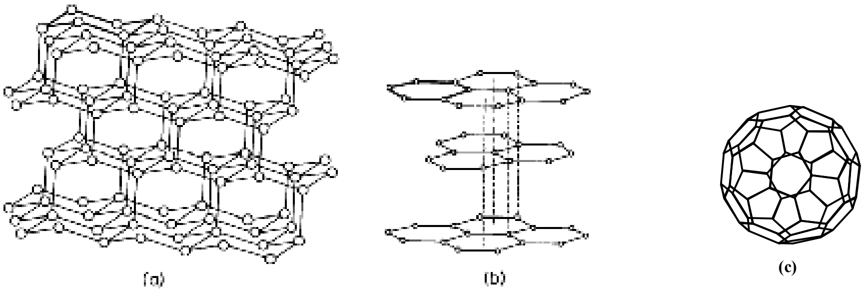


Figure 2. 1 The structures of (a) diamond, (b) graphite, and (c) buckminfulleren, C_{60} (Rao et al., 1995).

2.2 Carbon Nanotubes

Carbon nanotubes are known as carbon allotrope with tubular structure popularized by Iijima in 1991 (Iijima, 1991). It consists of one or more cylinders of graphitic shells where trivalent carbon atoms form a hexagonal network; i.e. each carbon atom is bounded to three neighboring carbon atoms through sp^2 hybridization. The carbon nanotubes that have one cylinder called as single-walled carbon nanotubes (SWNTs) and carbon nanotubes with more than one cylinder called as multi-walled carbon nanotubes (MWNTs).

The formation of CNTs resembles the rolling up of a graphene sheet into a direction. The different direction of rolling up gives different properties of CNTs. It is known structurally there are three types of CNTs such are zigzag, armchair, and chiral. Each cylindrical layer in CNTs of the three types can be expressed using formula:

$$r = \boldsymbol{a_1}n + \boldsymbol{a_2}m$$

In this case r stands for vector while $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$ are lattice basis as shown in Fig. 2.2. When m = 0 the CNTs is zigzag, when n = m the CNTs is armchair, and for $n,m \neq 0$ we call chiral type. Geometrically three types of CNTs represented in Fig. 2.3.

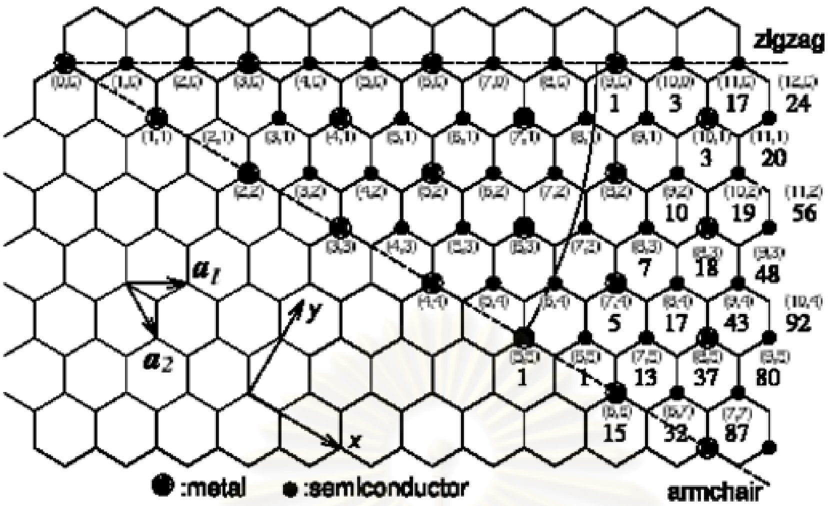


Figure 2. 2 Lattice vector in CNTs (Dresselhaus and Avouris, 2001).

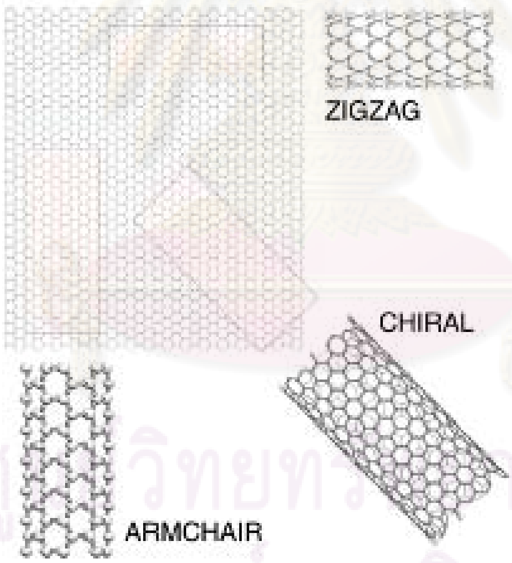


Figure 2. 3 A schematic image of a graphene layer and SWNT formed by rolling-up of rectangular strips of hexagonal graphite monolayers (Ruoff et al., 2003).

Many other observations have shown that carbon nanotubes have other intriguing properties, such as: (1) High flexibility, related to the ability of the carbon atoms to rehybridize, with degree of rehybridization depending on the strain. (2) High capability to sustain strain tension (40%) without brittleness, plastic deformation, or bond rupture. Their other extraordinary properties include a density of 1.4 gram/cc, compared with aluminum at 2.7 gram/cc; tensile strength of 45 billon pascals, while steel alloys break at 2 billion pascals; and the ability to carry 1 billion amps/cm^2, whereas copper wires burn out at 1 million amps/cm^2 (Marcell, 2006). The band structure of CNTs can be shown in Fig 2.4.

These features make the carbon nanotubes ideal candidates for reinforcing fibers in polymer-based composites. The use of carbon nanotubes as reinforcing systems of polymer matrix would offer several advantages over the conventional reinforcements, including continuous and short fibers (glass, carbon). The addition of carbon nanotubes to polymer could improve not only the mechanical properties, but also the thermal stability and the electrical conductivity of resulting composite.

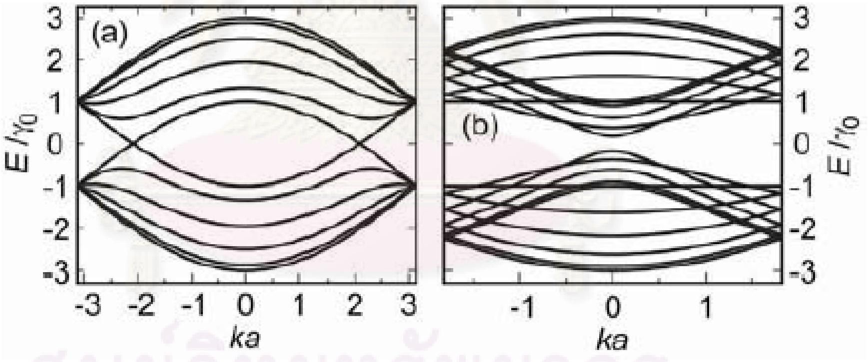


Figure 2. 4 Band structure of (a) a metallic (5, 5) CNT and (b) a semiconducting (10,0) nanotube (Freitag, 2006).

In recent years, many researchers have manufactured composite films from carbon nanotubes and polymer matrices, which may be either thermoset or thermoplastic. Table 2.1 lists samples made by various researchers to form this new class of composites (Shonaike and Advani, 2003).

Table 2. 1 Polymer based CNTs systems and corresponding dispersion methods.

Nanotubes	Polymer	Preparation method
SWNTs	Epoxy (epon 828)	Ultrasonic dispersion
SWNTs,MWNTs SWNTs	PMMA	Mixing in ultrasonic bath and spin coating, ultrasonic dispersion, mixing followed by in situ polymerization.
SWNTs	Polypropylene	Electrochemical method, mixing, and ultrasonic treatment
MWNTs	Epoxy (Araldite LY564)	Tube sonication, drying, and dispersion on a glass surface, spreading of polymer by blade.
MWNTs	Ply(vinyl alcohol)	Mixing with polymer, casting, and controlled water evaporation after chemical treatment of the tubes

In CNTs there were about 1/3 of the nanotubes are metallic and 2/3 are semiconducting (Dresselhaus and Eklund, 2000). Therefore CNTs could be metallic or semiconductor (Dresselhaus and Dai, 2004), (Quang et al., 2006). A semiconductor is a solid with an electrical conductivity between that of metal and insulator. This conductivity caused by electronic particle, such as electron, holes, and polarons, referred as carriers (of charge) which are set free by ionization or an electric field.

Table 2. 2 Electrical conductivities of come metals and non metals at room temperature.

Metals and alloys	Conductivity $(\Omega.m)^{-1}$	Non Metals	Conductivity $(\Omega.m)^{-1}$
Silver	6.3×10^7	Graphite	10^5 (av)
Copper, commercial purity	5.8×10^7	Germanium	2.2
Gold	4.2×10^7	Silicon	4.310^{-4}
Aluminum, commercial purity	3.4×10^7	Polyethylene	10^{-14}
		Polystyrene	10^{-14}
		Diamond	10^{-14}

The changes in electronic properties are controlled by external means such as light, applied voltage, magnetic field, and temperature (Boer, 1990). The range of conductivity (σ) various materials can be seen in Table 2.2. From this table it is seen that the pure metals silver, copper, and gold have the highest conductivity, about, 1×10^{7} Sm^{-1}.

2.3 Polymer in General

The term of Polymer came from Greek, where *poly* means many and *meros* means parts. The *mer* is the basic part and the basic building block is termed the *monomer*. Polymer materials can be categorized as either thermoplastics or thermosets. Thermoplastics can remelted after solidification, and thermosets solidify via a chemical reaction that causes polymer molecules to crosslink. These crosslink materials can not be remelted after solidification.

Because of multipurpose of polymer, a polymer seldom sold as a pure material. More often, a polymer contains several additives to aid during processing, add color, or enhance the mechanical properties (Oswald, 1998). This information enables one to modify the properties of polymer to be used as a sensor material.

Based on its conduction, materials might be divided into three groups. An insulator has conductivities in the range of 10^{-18} to 10^{-5} Sm^{-1}. A semiconductor is in the range of 10^{-7} to 10^{-3} Sm^{-1}, and a conductor is usually given as 10^{-3} to 10^{6} Sm^{-1} (Sperling, 2006). Therefore to determine the material sensor, the conductivity of material should be considered.

Basically, almost all polymers are insulator except very view of them are conductive such as poly(*p*-phenylene), polythiopene and derivaties, poly(phen-ylene vinylene), polypyrole and polyaniline (Carraher, 2003). Besides, properties such as the solubility and electrical nature of polymers, which depend on polymer structure, are intimately related to polarity (Ebewele, 2000). The more polar structures have lower resistivity. By use of sufficient carbon of high structure index in polymers, it is possible to increase considerably the electrical conductivity of soft rubber (Schmidt and Marlies, 1948). The same factors that increase relative permittivity decrease volume resistivities ρ: polar groups in polymer, high mobilities of chain segment, polar additives, and higher temperatures (Elias, 1997). Relative permittivities are low for apolar polymers (PTFE, PE), higher for polymers with polarizable groups (PS, PC), and still higher for polar material (dry PA). Resistivity thus decreases with increasing content of polar groups and increasing mobilities of chain segments. The resistivity (specific volume resistivity) of dielectric polymers decreases with increasing relative permittivity and finally becomes constant at $\varepsilon_r > 8$. Polar side groups and cristalinity both also increase thermal conductivity. Decreasing the temperature of a polymer also serves to decrease the inter-chain distance and increase the thermal conductivity.

Additives can often have a large effect on the thermal conductivity of a polymer. Usually the contribution of additive is in proportion to its weight percentage. The absorption of water vapor into an already polar polymer has produced a material approaching a semi conductor, but this is not easily maintained condition. A more promising route (Daniels, 1989) for production of a conductive material that still retains the characteristics of a polymer is in the direction of structural alteration.

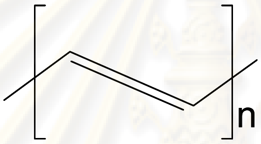
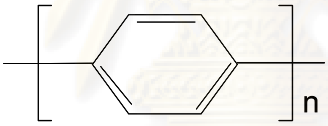
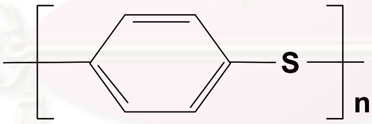
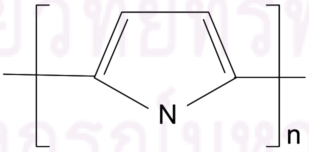
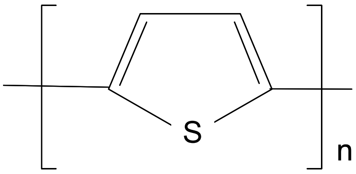
The addition of CNTs to polymers could improve not only the mechanical properties, but also the thermal stability and electrical conductivity of the resulting composite. Table 2.3 reports some examples of CNTs/polymer composites and the corresponding electrical conductivity (Shonaike and Advani, 2003).

Table 2. 3 Electrical conductivity of CNTs/polymer composites.

Nanotube content	Polymer	Composite electrical conductivity, Sm^{-1}	Pure polymer electrical conductivity, Sm^{-1}
0.1 vol%	Epoxy	10^{-2}	5×10^{-8}
20 wt%	Polypyrrole	1.4×10^{-1}	2.6×10^{-2}
20 wt%	PVOH	10^{-1}	2.9×10^{-9}
7-11 wt%	PMPV	1.5×10^{-9} to 1×10^{-1}	2×10^{-10}

In polymers the conjugated bonds plays role of electronic mobility. Adding a dopant such as halogens or alkaline metals into the polymers will increase the conductivity by order 10^{10} to 10^{7} Sm^{-1} (Akilah and Moet, 1990). Conjugated polymers during doping are partially oxidized (p-doped) or reduced (n-doped) with suitable reagents. Doping by AsF_5 raises the specific electrical conductivity of trans-poly(acetylene) from 10^{-7} to 12×10^{4} Sm^{-1} and of polyphenylene (p-phenylene) from 10^{-13} to 5×10^{4} Sm^{-1}. Table 2.4 lists of the conjugated polymers and dopants with their conductivity (Van Krevelen, 1990).

Table 2. 4 Double bond polymers with dopant.

Polymer	Structure	Typical methods of doping	Typical conductivity $(ohm\ cm)^{-1}$
Polyacetylene		Electrochemical, Chemical, AsF_5	500
Polyphenylene		Chemical (AsF_5)	500
Poly(phenylene sulfide)		Chemical (AsF_5)	1
Polypyrrole		Electrochemical	600
Polythiopene		Electrochemical	100

The doping of inorganic semiconductors such as GaP, InSb, or Ge generates quasi-free electron (n-carriers) or defect electrons (p-carriers) whereas the doping of suitable organic polymers leads to oxidation (p-doping) or reduction (n-doping) reactions. Ratio for dopants to repeating unit is 1:1 molar ratio.

The basic mechanism of electronic conduction is illustrated in Fig. 2.5. The importance of π-bonds in electronic conduction must be emphasized, as the overlapping electronic clouds contribute to the conduction. Strong interactions among the π-electrons of conjugated backbones are indicative of a highly delocalized electronic structure and large valence bandwidth. For good conductivity, the ionization potential (IP) must be small. The electron affinity, EA reflects the ease of addition of an electron to the polymer as shown in Fig 2.5, especially through polymer doping.

In polyconjugated system, (Mitchell, 2004) the π-orbitals are assumed to overlap, and they form a valence and a conduction band as predicted by band theory. If all the bond lengths were equal—that the band would overlap and the polymer would behave as a quasi-one-dimensional metal having good conductivity.

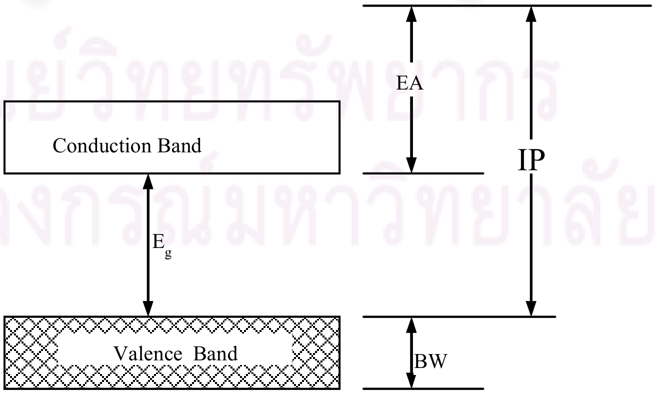
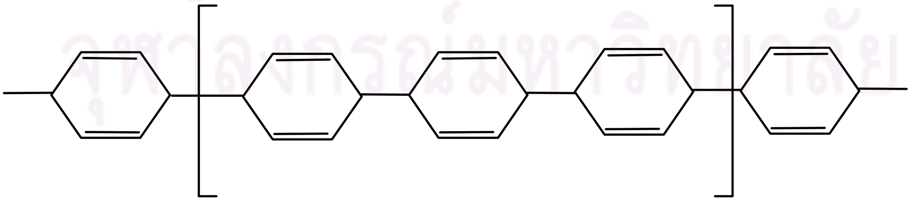


Figure 2. 5 Energy band of materials.

Bandwidth, BW, correlates with carrier mobility; a large bandwidth suggests a high intrachain, which favors high conductivity. Doping was assumed to remove electrons from the top of valence band, a form of oxidation, or to add electrons to the bottom of conduction band, a form reduction (Sperling, 2006).

When we consider electronic conduction solely in homogeneous polymers, band theory is not totally suitable because the atoms are covalently bonded to one another, forming polymeric chain that experience weak intermolecular interaction. Thus, macroscopic conduction will require electron movement, not only along chain but also from one chain to another. According to Elias (1997) electrical conductivity in polymers is assumed to be due to *solitons* or *polarons*. Fig 2.6 describes the soliton and polaron. In addition the most important condition for the existence of electrical conductivity in organic polymers seems to be the ability to form overlapping orbitals. The planar structure of trans-poly(acetylene) promotes the overlapping of its π and p orbitals

Soliton



Polaron

Figure 2. 6 Soliton and Polaron that in charge of electrical conduction in polymer.

The *soliton* is relatively stable electron with an unpaired spin and is located in a nonbonding state in the energy gap, midway between the conduction and valence bands. Therefore involving movement of electrons *intra*-molecullarly and *inter*-molecularly via the positive or negative soliton causes conduction occurs (Steven, 1999). In typical situation, the presence of these neutral solitons gives *trans*-poly(acetylene) the characteristics of intrinsic semiconductor with conductivity of 10^{-5} to 10^{-6} Sm^{-1}. The conductivity of poly(acetylene) can be magnified by doping. Exposure of a poly(acetylene) film to dry ammonia gas leads to a dramatic increase in conductivity of 10^{5} Sm^{-1} (Mitchell, 2004).

The deformed section of lattice and the charge carrier then form a species called a *polaron*. Unlike the soliton, the polaron cannot move without first overcoming an energy barrier so movement is by a hopping motion (Mitchell, 2004).

Although complete understanding of the conduction mechanism remains elusive, certain structural features are known to influence the level of conductivity. These include:

1. Delocalization. An extended conjugated system is usually necessary for backbone conductivity; however, charge may be transferred in some cases through pedants group.
2. Doping. Dopants may be electron acceptors such as arsenic pentafluoride or halogen, or electron donor such as alkali metal. Conductivity varies with dopant concentration. Doping may also effect rearrangement of the double bond of conjugated polymers into a conjugated conduction mode.
3. Morphology. Conduction is influenced by configurational and conformational factors, as well as crstallinity. Conduction of polyacetylene film in the direction of molecular alignment is increased significantly by stretching. (Saunders, 1997)

2.4 Composites

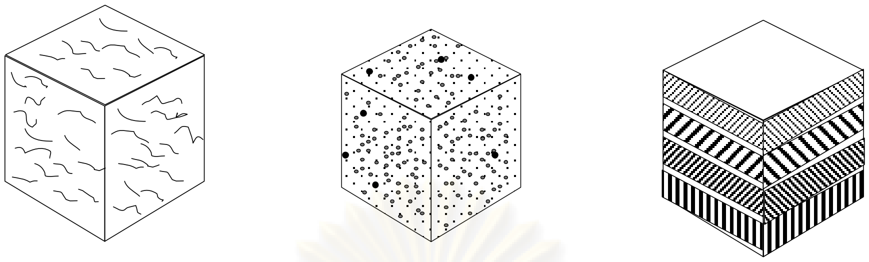
2.4.1 Structural of Composites

A composite is a combination of material from different categories, such as metal, ceramic, and polymer, or even different material within each category, in such a way as to achieve properties and performance that are unique (Mitchell, 2004). In another definition: a composite is material evolved from the simplest mixture of two or more material to obtain a property that was not there (Schawartz, 1997). Therefore the composites also called “engineered materials” (Schaffer et al., 2006).

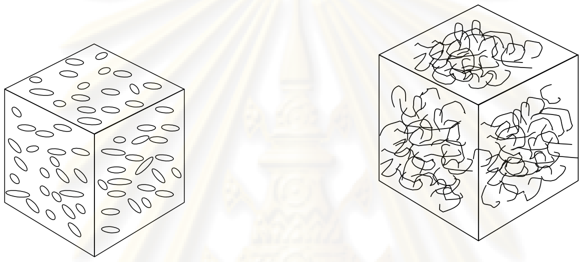
In a composite there are parts called *reinforcing phase* and other material called *matrix phase*. The matrix phase is continuous phase that surrounds reinforcing phase or dispersed phase (Callister, 2003). There are five general types of composite (Micthell, 2004) when categorized by bulk form as shown in Fig. 2.7 such as fiber composite, particulate composite, laminar composite, flake composite, filler composite. Practically, however, there are four type composite based on the material such as: metal-matrix composite (MMCs), polymer-matrix composite (PMCs), ceramic-matrix composites (CMCs), and carbon-carbon composites. Recently there is a term called nanocomposite means to distribute as much as possible amounts of nanoparticles in a polymer matrix. It seems that the composite of carbon nanotubes/PPP categorized in particulate composite.

The use of nanoparticles as reinforcement in polymer is a common method to improve the mechanical and/or electrical properties of composites. The improvement of the fracture mechanic properties by addition of particles can be achieved when a sufficiently good interaction between nanoparticles and matrix polymer take place and when the particles are well dispersed within the matrix.

Currently there is a term nanocomposites means to distribute as much as possible amounts of nanoparticles in a polymer (Friedrich et al., 2005). These type of composites become a focus of scientists around the world since nanoparticles have different properties compared to macroscale.



Fibre composite Particulate composite Laminar composite



Flake composite Filled composite

Figure 2. 7 Classification of composites.

Various approaches for the fabrication of carbon nanotubes/polymer composites could be classified as (Olek, 2006):

a. Solution processing of composites: The most common method based on the mixing of the CNTs and a polymer in a suitable solvent before evaporating the solvent to form a composite film. The dispersion of components in a solvent, mixing, and evaporation are often supported by mechanical agitation (e.g. ultrasonication, magnetic stirring, shear mixing).

b. Melt processing of bulk composites: This method concerns polymers that are insoluble in any solvent, like thermoplastic polymers. It involves the melting of the polymers to form viscous liquids to which the CNTs can be added and mixed. Melt processing of composite fibers: CNTs are added to the melts of the polymers. The formation of CNT/polymer fibers from their melts occurs through e.g. the melt-spinning process.

c. Composites based on thermosets: A thermoset polymer is one that does not melt when heated such as epoxy resins. The composite is formed from a monomer (usually liquid) and CNTs, the mixture which is cured with crosslinking/catalyzing agents.

d. Layer-by-layer assembly (LBL): CNTs and polyelectrolytes are used to form a highly homogeneous composite, with a good dispersion, good interpenetration, and a high concentration of CNTs. This method involves alternating adsorptions of a monolayer of components which are attracted to each other by electrostatic interactions resulting in a uniform growth of the films.

e. In-situ polymerization: The polymer macromolecules are directly grafted onto the walls of carbon nanotubes. This technique is often used for insoluble and thermally unstable polymers which cannot be melt processed. Polymerization occurs directly on the surface of CNTs.

2.4.2 Mixing of Solids/Polymers

The involving of reinforcement phase in matrix phase carried out by dispersing of solids through a dispersant. In case of polymers as matrix, a dispersant could act as a solvent encompass surfactant or solvent encompass binder depending on the property of the dispersant.

There are terms are frequently confusing when mixing processing applied for solids. The terms are such as binder, dispersant, solvent, and surfactant. The following definition (Lewis, 1993) might be a reference to understand the meaning of the terms.

Binder: any cementitious material that is soft at high temperature and hard at room temperature, used to hold dry powders aggregate together.

Dispersant agent: a surface active agent added to a suspending medium to promote uniform and maximum separation of extremely fine solid particles often colloid size.

Solvent: a substance separable of dissolving another substance (solute) to form uniformly dispersed mixture (solution) at molecular or ionic size level.

Surfactant: any compound that reduce surface tension when dissolved in water or water solution, on which reduces interfacial tension between a liquid and solid.

In fact, the steps of fabrication of sensor material since mixing step of the materials up to coating step of composite onto electrodes give different meaning. A typical example is the fabrication of a sensor material consisting of MWNT/polymer. When the dispersant can make compact all the particles the dispersants have been acted as binder (Horn, 1955). When the polymer as matrix is dissolved by dispersant, at that time the dispersant acts as solvent. The dispersants could be considered as surfactants or adhesive agents when the dispersants enable composite adhered to surface of electrode.

2.4.3 Solvents for Polymer

Commonly solvents could be classified as following (Bart, 2005):

a. Nonpolar solvents (such as hexane and chloromethane)
b. Solvents of low polarity (such as toluene and chloroform)
c. Aprotic dipolar solvents (such as acetone and N,N dimethylformamide). An *aprotic Solvent* is an organic solvent that does not exchange protons with a substance dissolved in it.
d. Protic and protegenic solvents (such as ethanol and nitronethane). A *protic solvent* is a solvent that has a hydrogen atom bound to an oxygen as in a hydroxyl group or a nitrogen as in an amine group. A *protogenic solvent* is a

solvent capable of acting as a proton (hydrogen) donor strongly or weakly acidic (as a Brønsted acid).

e. Basic solvents (such as pyridine and 1,2 diaminoethane)
f. Acidic solvents (such as 3-methylphenol and butanoic acids)

Polymers may be distinguished on the basis of their solubility:

a. Polymers completely soluble in organic solvents (e.g. polystyrene)
b. Polymers which do not completely dissolve in organic solvents but swell sufficiently to allow extraction (e.g. low density polyethylene (LDPE), polypropylene).
c. Polymers almost completely insoluble in organic solvents (e.g. polytetrafluoro-ethylene (PTFE)).
d. Water-soluble polymer

2.5 Poly(p-phenylene)

As known over the last decade, conjugated polymers, e.g., poly(para-phenylene) (PPP), poly(para-phenylene vinylene)s, and polythiophenes, can be utilized as the active medium in organic light-emitting diodes (LEDs), light-emitting electrochemical cells, solar cells, photo detectors, lasers, field effect transistors, and all polymer-integrated electronic circuits. Many efforts has been devoted to obtain real applications of poly(p-phenylene) as a stable blue electroluminescence (EL). The generation of blue light is of crucial importance for red–green–blue (RGB) full color light-emitting devices. Moreover, it can be transformed into red and green light by internal or external color conversion (List and Scherf, 2007).

One weakness, however, of PPP is characterized by its total insolubility in common organic solvents. Until today, no applicable route toward high-quality, defect-free PPP films is known. Therefore, the approaches that have been investigated in the past include the use of soluble, nonconjugated precursor polymers and the electrochemical polymerization of benzene. The solubilization of PPP-type polymers was possible by the introduction of alkyl, alkoxy, ester, keto, or ionic side groups in a ‘‘hairy rod’’ approach as can be shown in Figure 2.8. Another typical of PPP-type polymer can be shown in Figure 2.9 (List and Scherf, 2007).

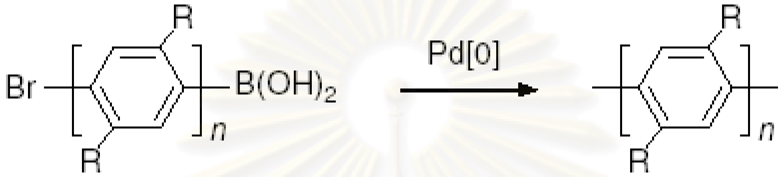


Figure 2. 8 Initial synthesis of poly(2,5-dialkyl-1,4-phenylene) after Schluter and Wegner (for solubility reasons—R represents longer n-alkyls with n: 6–12).

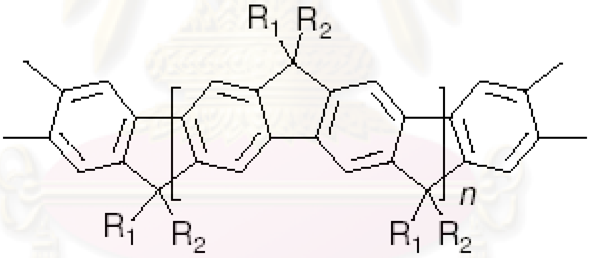
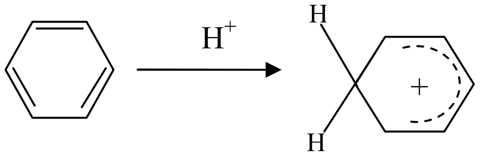


Figure 2. **9** Structure of a para-phenylene ladder polymer (LPPP).

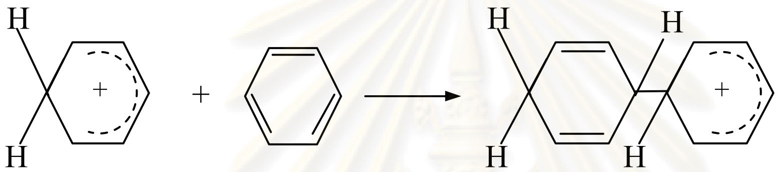
Since the chemical structure of PPP has double bond that means PPP might be used as sensor materials. In fact, however, the polymer is not available commercially. Hence to use PPP, the polymer must be synthesized. At least there are two methods available to synthesize the poly(*para*-phenylene) or PPP (Saunders, 1997). First method is polymerization of 1,3-cyclohexadiene with Ziegler–Natta catalyst, and second one to use benzene to make polymerization. Due to the benzene is easily to find and cheaper, it is possible to use the second method. The steps of the polymerization reaction follow step below.

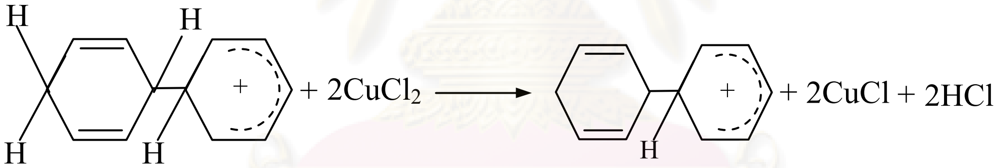
Initiation

$$AlCl_3 + H_2O \rightarrow [HOAlCl_3]^-H^+$$

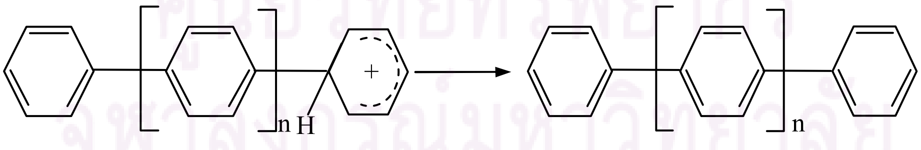


Propagation





Termination



Polyphenylene

2.6 Conductivity and Resistivity

The resistance (R) of a material has correlation with its conductivity. When a material has good conductivity that means its resistance is low and reversely. The correlation can be expressed as below.

$$R = \frac{\ell \rho}{A} \tag{1}$$

Where

R= Resistance, Ω

ρ = resistivity, $1/\Omega$

l = length, m

A= cross sectional area, m^2.

When sensors work at a range temperature the conductivity of materials will change. The changing can be estimated by its resistivity as can be expressed in eq. (2) (Smith, 2006)**.**

$$\rho_T = \rho_o{}^o{}_C\,(1+\alpha_T T) \tag{2}$$

Where

$P_o{}^o{}_C$ = electrical resistivity at 0^oC

α_T = temperature coefficient of resistivity, K^{-1}

T = temperature of metal, K

Due to mixing some properties of the material might be altered. For electrical properties, the altering conductivity of material can be represented by an equation as follow:

$$\rho_i = Ac_i(1-c_i) \tag{3}$$

where A is a composition-independent constant that is a function of both the impurity and host metals. As illustrated, typical of the influence of nickel impurity addition on the room temperature resistivity of copper is demonstrated in Fig. 2.10. (Callister, 2003).

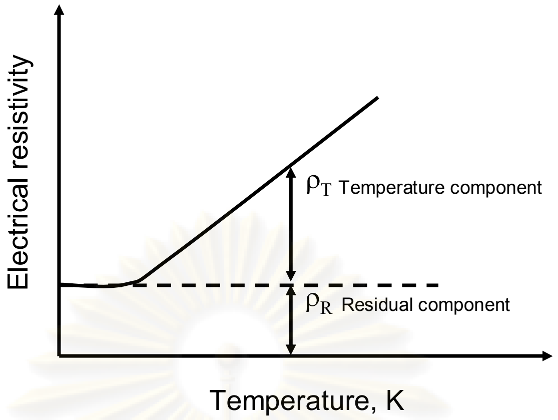
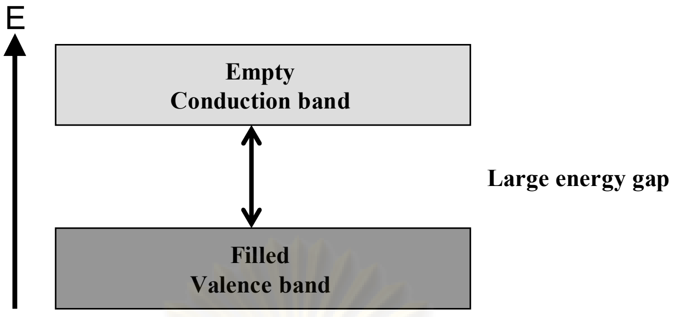


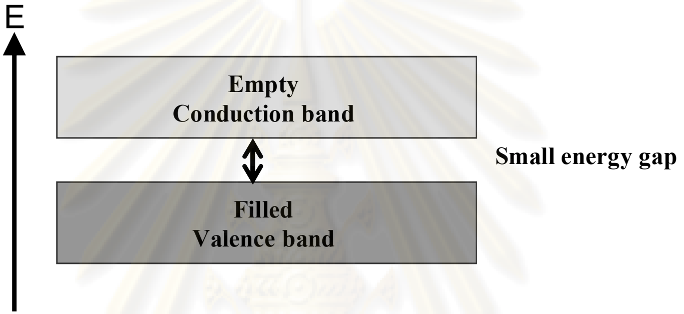
Figure 2. 10 Typical resistivity of copper.

To understand the mechanism of electrical conduction in a material it need to consider the energy-band model of electrons. There are three types of energy band related to conduction of electrons. Globally the schematic of energy-band model can be seen in Fig. 2.11. In this case, the electrons at higher energy level may descend to the lowest level. Fig. 2.11 shows the schematic of energy level in single atom.

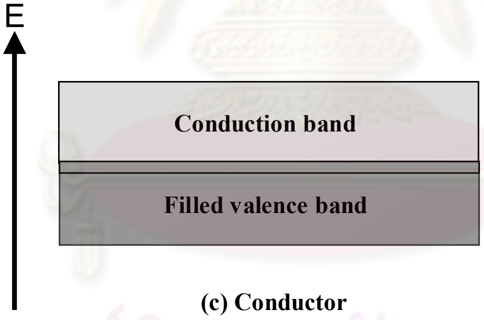
In Fig 2.11a the valence electron needs large energy to reach conduction band. The term "band gap" refers to the energy difference between the top of the valence band and the bottom of the conduction band. In other word the band gap energy is the energy needed to break a bond in an element. When a bond is broken, the electron has absorbed enough energy to leave the valence band and "jump" to the conduction band. In semiconductor materials, Fig. 2. 11b, the electrons gain energy at elevated temperature. The width of the band gap determines the type of material (conductor, semiconductor, and insulator).



(a) Insulator



(b) Semiconductor



(c) Conductor

Figure 2. 11 The schematic of energy band for materials.

2.7 Sensor

Until now the definition of sensor is not so clear. There are several definitions to explain what the meaning of sensors. Sometimes, the term of sensor is confused by transducer. Stevenson expresses that

> The American National Standards Institute (ANSI) standard MC6.1 defines a transducer as "a device which provides a usable output in response to a specific measurand" (Instrument Society of America, 1975). An output is defined as an "electrical quantity," and a measurand is "a physical quantity, property, or condition which is measured." In 1975, the ANSI standard stated that "transducer" was preferred to "sensor." However, the scientific literature has not generally adopted the ANSI definitions, and thus currently "sensor" is the most commonly used term.

According to Nice, 2004:

> Transducer is generally defined as a device that converts a signal from one physical form to corresponding signal having a different physical form. For an example transducer is a microphone.
>
> A sensor is generally defined as an input device that provides a usable output in response to a specific physical quantity input. The physical quantity input that is to be measured called the measurand, affects the sensor in a way that causes a response represented in output.

Fraden defines:

> A sensor is defined as a device that receives and responses to a signal or stimulus. The stimulus is the quantity, property, or condition that is sensed and converted into electrical signal. It can be said that sensor is a translator of generally non-electrical value into an electrical value.

2.8 Gas Sensor

The definition of gas sensor as defined by Wikipedia is a device which detects the presence of various gases within an area, usually as part of a system to warn about gases which might be harmful to humans or animals. Other source defines that a sensor is a device whose output can be quantified and changes with one or more physical phenomena. This output information can be used for process monitoring and control. A sensor likes a nose. When humans or animals use nose to detect an existence of a gas or aroma of something, a sensor works resemble. In other word the sensor is an imitation nose.

According to Yamazoe and Miura (1992) that the gas sensor should have two basic functions i.e. to recognize a particular gas (receptor function) and another function signal function (transducer function). The receptor function is a capability to make interaction between sensor material and gas sensed. The transducer function is the response which can be read from sensor material. In addition, as discussed by Simon et al. (2001), in a commercial system the sensor comprise of three main parts such as receptor, transducer, and operation system. A receptor is a part of sensor which deal object to be sensed. The measurement of physical variables associated with the resulting form of response allows estimation of the physical variables associated with the input energy. The operation system is intended how to quantize the response of receptor.

2.9 Several Terms in Sensor Study

There are several terms that should be understood when reading the discussion of sensors. The terms below are adapted from (labautopedia.com), (customsensorsolutions.com), and (nap.edu).

Analyte: a chemical species targeted for qualitative or quantitative analysis.

Baseline: a reference set of data against which operating data is compared or the electrical signal from a sensor when no analyte is present, but under otherwise "standard" conditions.

Response: the time taken by a sensor to approach its true output when subjected to a step input is sometimes referred to as its response time. It is more usual, however, to quote a sensor as having a flat response between specified limits of frequency. This is known as the frequency response, and it indicates that if the sensor is subjected to sinusoidally oscillating input of constant amplitude, the output will faithfully reproduce a signal proportional to the input.

Response time: this is the time required for a sensor to respond to a step increase in the analyte gas. Since most sensors approach the final signal asymptotically, response time is usually defined as the time needed to reach 90% of the final signal (for a given concentration of gas).

Recovery time: the time required for a sensor to return to baseline after a response to an analyte. It is usually expressed as the time for the signal to fall below 10% of the maximum response.

Sensitivity: the smallest change in a physical quantity or parameter that can be detected by a measuring system. Determined by signal to noise ratio, system amplification and / or quantizing limit

2.10 Materials for Gas Sensor

A material is sensitive to a kind of gases might not be sensitive or slightly sensitive to other gases. This part discusses achievements in the application of several materials for gas sensing based on reports from journals and other publishing media.

2.10.1 Semiconductors

Xu et al. (2006) studied the using of zinc oxide (ZnO) to detect chemicals such as ethanol, acetone, toluene, benzene, and xylene. In their work they used two type of ZnO i.e. ZnO nanoparticles and ZnO porous nanosolid. The sensor materials were pasted onto alumina tube then exposed to chemicals at different temperature. As a result ZnO porous nanosolid shows comparatively high performance than another. In different method Lee et al. (2005) used semiconductor of tin oxide (SnO_2) to study sensor material. They also prepared two type of sensor material with same based. C-SnO_2 and P-SnO_2 were named to both of materials where the first came from commercially and the second from precipitation of $SnCl_4$. The substrate they used was alumina on which one side as a place to paste sensor material and another side as heater. After exposed to chemicals, the two materials show different sensitivity. In this case we can not say which one is better because at different condition the materials give different sensitivity. As to improve the using of SnO_2, Triantofyllopoulou et al., 2008 added Pd on SnO_2 then exposed to NH_3 gas. Within low concentration of NH_3 the material shows relatively high sensitivity at 280°C.

Using tungstic acid powder Srivastava and Jain (2008) prepared sensor material WO_3 by sol-gel method. The authors described the fabrication of low cost ammonia sensors by using screen-printing technology. The material pasted onto alumina substrate attached heater and electrode fingers then sintered at 800°C. As comparison the material doped with Au, Pt, and Pd. After exposed to NH_3, WO_3 doped by Pt shows better sensitivity compared to other doping agents.

In humidity case, Jain et al. (1999) tried to use the combination of two metal oxides such as zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2). With composition 50% of the material and Li^+ as doping agent, the authors successfully detect the humidity in all range. They also deduced that sintering of material at high temperature influences material sensitivity.

2.10.2 Polymer and Carbon

The combination of CNTs and polymer as a composite for sensor material might be seen from report of Valentini et al. (2003). They reported that the polymer positioned onto CNTs grown on Si_3N_4 has potential to be sensor material. As shown the authors work, the conjugated polymer (poly(3-octylthiophene)–P_3OT) on the CNTs has conductivity tend to decrease as temperature increase. The schematic of the sensor material can be seen as follow.

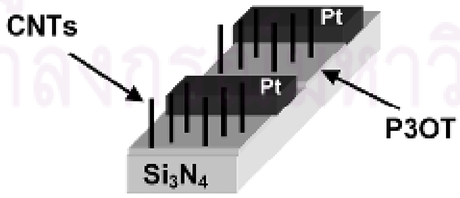


Figure 2. 12 An electrode from silicon (Valentini et al., 2003).

In the work reported here, Li et al. (2007) used nine regioregular polythiophene (rr-PTs) based polymers with different side chains, end-groups and copolymers. After fabrication the composite they were characterized by measurement for 10 different volatile organic compounds (VOCs). The results show that end-group involving in matrix influences the sensitivity of sensor. When the exposed gas has similar group with compound in matrix the interaction of induced van der Waals push molecules closer then reduce charging hoping.

Arab et al. (2006) reported that MWNTs grown onto Si wafer can detect several chemical vapors. They used the vertical growth of aligned carbon nanotubes on structure surfaces composed by a set of Ni electrodes and SiO_2 surfaces fraction. The results show that carbon nanotubes could be efficient in terms of sensibility for detection of pollutant species like NH_3 even at ambient temperature.

In their paper Yu et al. (2006) used multiwall carbon nanotubes (MWNTs) pasty pasted onto glass substrate. Then the glass substrate dipped coating in poly(ethyleneimine) containing 1 wt% water. Using the method, the authors got the sensor material. To be effective they made 60-layer of sensor material on substrate to sense the humidity. As a result the resistance increases over the range of 5–97% relative humidity (RH), and, especially, almost linearly in the range of 5–85% RH.

Athwale et al. (2006) reported that a Pd–polyaniline (Pd–Pani) nanocomposite has been utilized as a sensing material for various alcohol vapours. The synthesized Pd–polyaniline nanocomposite was packed into pellets (diameter 12 mm, thickness 3 mm) by applying a pressure of 7 tonnes with the help of a Pye–Unicam system. The sensing measurements were performed by exposing the sensor (as pellets) to alcohol vapors in a close glass container. A Pd–Pani nanocomposite was found to be a highly sensitive and selective sensor for methanol vapors.

Jouve et al. (1995) in their paper reported the gas-sensing properties of devices using a composite polymer thin film coated onto a glass electrode as shown in Fig. 2.13. This composite is constituted by a polyethylene matrix in which are included crystalline metallic salts (tetrathioful-valinium tetracyanoquinodimethane TIT-TCNQ). The sensor material was deposited on indium tin oxide (ITO) conductive glass. The structures exhibit interesting responses to absorption in terms of magnitude (NO_2, humidity), reversibility (CO_2, O_2 or humidity) and response time (CO_2).

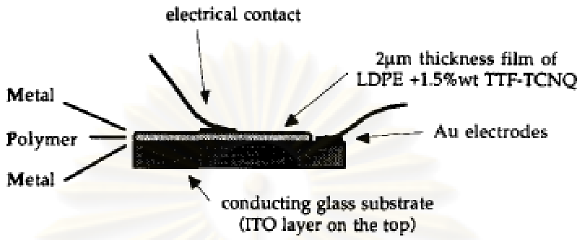


Figure 2. 13 An electrode from glass (Jouve et al., 1995).

The preparation of sensor material from PPY is presented by de Melo et al. (2005). The method conducted by dissolved polymer in ferric chloride solution previously prepared using appropriate solvents. Then the pasty deposited onto ITO-substrate. The sensor composite produced then tested using various chemical vapors. The sensitivity testing shows that each composite has own sensitivity depending on the vapor targeted. They key words of author conclusion are apolar and polar vapor.

The potential of carbon black as filler in polymer is presented by a report of Quercia et al. (2005). The authors used dispersion method to be involved filler in polymer. A surprised result, that the combination of poly(methyl methacrylate) (PMMA) and a kind of carbon black (CB) as filler show relatively better sensitivity than CNTs as filler. The explanation of this result addressed to affinity between matrix and solvent targeted. Similarly, but using complex dissolution Zeng et al. (2007) used CB and polymer to get the CB/β-CD-block-PDEA copolymer composites. The sensor material fabricated exhibits sensitive to CH_2Cl_2, $CHCl_3$, benzene, and tetra hydro furan (THF) vapor.

Arshak and Gaidan (2006) investigated an array of thick-films gas sensors made from polymer, iron oxide and manganese oxide. The first step was preparation of iron and manganese oxide followed by mixing 5% polyvinyl butyral (PVB). Then the CB dissolved into the solution. Next films were printed onto glass substrates with silver electrodes. The sensor material with certain composition was more sensitive to alcohols and toluene.

It was reported that the introduction of electron donating groups to the tetraphenyl-porphyrins ($TPPH_2$) molecule enhanced its sensitivity, probably due to the increase of the electron density or basicity at the central nitrogens. In this study, Itagaki et al. (2005) used $TPPH_2$ and its OCH_3, OH and COOH substituted derivatives dispersed in an ethyl-cellulose (EC) matrix to form a porphyrin–polymer composite film. In their method EC and porsphyrins were dissolved in ethanol/toluene mixture (8:2) followed by addition of plasticizer. The composite produced then deposited onto alumina substrate. Exposing to NO_2 and SO_2 gas result the sensor material has relatively high sensitivity to NO_2 than another.

The metal oxides films are widely used for CO, aromatic hydrocarbon and NO_2, gas-sensing applications, but such sensors mostly lack selectivity and operate at high temperatures (300–500 ^{o}C). Ram et al. (2005a) focused on the use of organized ultrathin films of conducting polymers and their nanocomposites. Two approaches of fabrication sensor material were conducted such as layer-by-layer or in situ self assembled film of polymer and nanocomposite of SnO_2/polymer. Through consecutives step of fabrication the authors finally got the sensor material and test it. The authors conclude that the regiorandom-polyhexylthiophene (rr-PHTh)/SnO_2 composite have a good potential to recognize NO_2 in ppb concentration. Based on this experience, Ram et al. (2005b) made an attempt to fabricate CO gas sensor using highly organized ultrathin films of polyaniline (PANI) nanocomposite. Their approach focuses on the fabrication, characterization and application of PANI–SnO_2 and PANI–TiO_2 nanocomposite film for CO gas sensing application. As a result, PANI-SnO_2 seems comparatively high sensitivity than another when exposed to CO. Then Tai et al. (2008) reported that polyaniline/titanium dioxide (PANI/TiO_2)

nanocomposite thin films could be used as sensor material. PANI/TiO_2 nanocomposite thin films were synthesized by in situ self-assembly technique in the presence of colloidal TiO_2 with a dip-coater. The material then deposited onto silicon substrate. The exposing NH_3 on sensor material exhibits sensitivity of the PANI/TiO_2 composite, which also exhibited good reproducibility, selectivity and long-term stability.

Tillman et al. (2003) successfully enhanced sensitivity towards volatile carboxylic acid vapors. The sensor material consists of linear poly(ethylenimine) (*l*-PEI) and CB with ethanol as dispersant. The material deposited onto insulating substrate. The results exhibit that exposed to acetic acid vapor pushes high sensitivity. The less content of CB in polymer response of composite will be low. Using CB-based Li et al. (2003) focused on the response performance of carbon black filled polystyrene composites various organic vapor environments. The polystyrene composites studied in their work are synthesized by in-situ polymerization of styrene at presence of carbon black particulates. CB content and type of vapor are among the factors which are influencing the performance of material sensor.

Dong et al. (2004) investigated electrical resistance responses of amorphous polymer composites against various organic vapors at low concentrations. The sensor material was fabricated using polymerization-filled carbon black to produce carbon black/poly (butyl methacrylate) (CB/PBMA) composite. The sensor material deposited onto glass strip on which two copper wires interval 1 mm attached. The experimental results indicate that the composites have high selectivity to various organic vapors. In addition, composites can be used as a novel organic vapor sensor to detect, quantify and discriminate various organic vapors.

Hu et al. (2004) considered that the coexisting nonpolar and polar segments on polyurethane chains will be quite sensitive to organic solvent vapors regardless of their polarities as characterized by the drastic changes in conductivity. To prove this assumption the author employed carbon black (CB) as filler in waterborne polyurethane (WPU). The composite then deposited onto epoxy substrate then put inside a conical flask. Using eighteen solvent vapors, the sensor material exhibit its sensitivity to both polar and non-polar vapor. In their report, Chen et al. (2005) used same composite and method as previous to investigate the effect of temperature and vapor pressure on sensitivity. There were more than ten solvent vapor with different polarity exposed to the sensor material. As a conclusion, that at a given temperature, maximum of responsivity decreases when vapor pressure decreases. As to continue their work, the authors (Chen et al., 2006) reported the using of same composite such as CB/WPU composite. However the authors focus on the influence of both crosslingking and uncrosslingking in sensitivity. The crosslinking of the composite fabricated by addition Isophorone diisocyanate (IPDI) onto the CB/WPU composite. Exposing to solvent vapor shows that crosslingking CB/WPU composite more sensitive than uncrosslingking. While with other polymer Kim et al. (2007) presents a bubbler-based sensor measurement system that allows timed flow injection of gaseous volatile organic compounds (VOCs) in a wide analyte concentration range. The sensor material comprise of carbon black (CB) filled poly(vinyl pyrrolidone) (PVP) and poly(methyl methacrylate) (PMMA) were put inside a measurement system. By using the bubbler with a perforated ceramic disk, the analyte flux be regulated over a wide concentration range. The generated analytes were efficiently diluted by two-step dilution process, and delivered into a detection chamber. To employ CB and to prepare a novel gas sensor with selective sensitivity, Zeng et al. (2007) fabricated carbon black (CB)-filled waterborne-cyclodextrin-blockpolydiethylene glycol hexandioic ester copolymer (abbreviated to waterborne β-CD-block-PDEA copolymer) composites. In the sensitivity measurement the author used similar method conducted by Chen et al. (2006). The author found that electric resistance of the composites remarkably increased upon exposure to vapors of low permittivity (like chloroform and tetrahydrofuran), while nearly no response can be detected to vapors of high permittivity (like water and methanol). What is more interesting is that the composite maximum responsivity was correlated to the molecular size of vapors of low permittivity on a half-logarithmic scale.

On the basis of conductivity networks analyses, Li et al. (2006) presented their work focused on the evaluation of the interfacial interaction in carbon black filled amphiphilic tri-block copolymers of polystyrene-b-poly(ethylene glycol)-b-polystyrene (PSPEG-PS). The sensor material produced exhibit sensitivity on several solvent vapors. In this case activation energy on interface is independence to CB content.

Studies have shown that different materials of sensor electrodes affect the properties of sensor devices. Ma et al. (2006) made polythiophene composite film formed via in situ polymerization at room temperature. The sensor material deposited onto interdigital carbon electrodes immersed into the monomer–oxidant contained mixture of a small amount of boron trifluoride etherate. Examinations on the gas sensitivity of polythiophene composite film to a series of vapors were carried out. It was found that the film showed good sensitivity to ammonia, as well as fast response and good reproducibility.

Surface modification of the carbon nanotubes plays an important role for their utilization in various applications. Therefore Vedala et al. (2004) in this study produced single-wall and multiwall nanotubes by grown on a 1 cm^2 silicon dioxide substrate using chemical vapor deposition (CVD). The surface of grown nanotubes was modified by polyvinyl alcohol (PVOH) and the wettability on nanotubes. This fictionalization tends to change the surface of nanotubes into hydrophilic thus increasing its sensitivity.

It is reported that Zhang et al. (2006) discussed a new class of conductive composites with good gas sensitivity was fabricated by filling polystyrene with vapor grown carbon nanofibers (VGCNF). Polystyrene and VGCNF were mixing using sonication. Then the composites were deposited onto glass substrate. Finally to measure the sensitivity, the glass substrate put in a sealed glass vessel. The AVGCNF (6.25 wt.%)/polystyrene composite shows good candidate for gas sensor. Similarly, carbon nanofiber (CNF)/polypyrrole (PPy) coaxial nanocables were successfully fabricated via one-step vapor deposition polymerization (VDP) by Jang et al. (2007). The author’s motivation of this study is to deposit a uniform and ultrathin PPy layer onto the CNF surface by one step VDP method and to investigate the feasibility of

CNF/PPy coaxial nanocables as a highly sensitive sensor. Gases recognized were NH_3 and HCl.

There is a vast literature associated with the use of carbon nanotubes (CNTs) or carbon nanofibers (CNFs). Li et al 2008 reported their study about the gas-sensing properties of two GCNF– polymer brushes, GCNF–poly(*n*-butyl acrylate), GCNF–PBA and GCNF–poly(acrylic acid), GCNF–PAA. Based on sensing measurement, detection NH_3 using GCNF-PAA composite occurs almost 1000 times compared to detection to other chemical vapors.

In this paper Mill et al. (2007) applied their original concept of micro resistor sensor (μR) and quartz crystal microbalance (QCM) sensor to measure changes in mass and volume, in response to different odorants. First of all polymer solution was prepared followed by mixing with CB using sonication. Then the pasty was deposited onto μR and QCM. Comparison of the magnitude of the response of the sensors with the thickness of the polymer film in each case suggested that the response of the QCM sensors was linked to the polymer thickness, whereas that of the μR sensors was independent of thickness.

It is known that a kind of polymer poly(3,4-ethylenedioxythiophene)/poly-(styrene sulfonate) (PEDOT/PSS) received sustained interest in recent years as one of the most stable conducting polymers. Hence, Dan et al (2007) measured the electronic properties and gas sensing response of nanowires containing segments of PEDOT/PSS. Considering the results of sensitivity the sensor material has good sensitivity to the analyte, rapid response and recovery, and excellent reproducibility, both in time and between samples, under ambient conditions.

The aim of Sartore (Sartore et al., 2005) in their work is the development of vapor detectors formed from composites of conductive carbon black and insulating organic multifunctional polymers having metal ions complexing ability. The polymer-based in the author work was poly(amidoamine)s (PAAs). The all composites were deposited onto quartz microbalance (QCM). Based on sensitivity measurements, the sensor material is relatively high sensitive to amines group.

This paper describes a high-performance system set-up for measurements with gas sensitive polymeric layers. Fort et al. (2005) deposited the polymeric films on prototypal quartz crystal microbalance (QCM) sensors that allow both quartz frequency resonance variation and polymer resistance measurements. The polymer were poly(3,3’-dipentoxy-2,2’-bithiophene) (dimmer) and poly(3,3’-dipentoxy-2,2’:5,2”-terthiophene) (trimmer) with different dopants. The results exhibit its sensitivity to alcohol vapor and CO gas.

Kulkarni et al. (2006) reported the using of Poly(*N*-methyl aniline) (PNMA), doped with different acids (viz. HCl, $HClO_4$, H_3PO_4, H_3BO_3 and acetic acid). After synthesizing by a chemical polymerization method using ammonium persulphate as an oxidizing agent, the sensor material fabricated in pellet form. For testing the authors put the pellet in a glass chamber. As a result the PNMA doped by H_3PO_4 was the best sensing response compared than other dopants.

In this paper Santhanam et al., (2005) reported the utilization novel nanocomposite material made up of multiwalled carbon nanotubes and poly (3-methylthiophene) which is sensitive to chloromethanes. The 3-methylthiopene was mixed with MWNTs which previously functionalized. The solution then added by polyethylene oxide followed by dropping acetonitrile to get pasty. Sensitivity measurement conducted by deposited pasty onto polymer substrate. In fact, the material sensor can discriminate between methane and chloromethane.

In the present work, Chen et al., (2005) fabricated a composite of polypyrrole (Ppy) and MWNTs. In this work, the authors used vapor phase polymerization to fabricate the sensor material. A glass substrate with gold electrode was used to put the sensor material. The gas sensitive characteristics of the composite to NH_3 vapor over a wide range of concentrations were investigated at room temperature, and the effect of the oxidizing agents and dopants on its sensing behavior was also studied. Three type sensor materials were prepared such as pure MWNTs, pure PPy, and composite. As a result that the composite shows a higher sensitivity than both Ppy and MWNTs separately in the detection of NH_3 vapor over a wide range of concentrations at room temperature.

In this paper, Horrillo et al., (2004) compares the obtained experimental results with surface acoustic wave sensor (SAW) devices coated with three different polymers, polydimethylsiloxane (PDMS), polybutadiene (PBD) and polyetherurethane (PEUT). The composites were deposited on quartz substrate (9 x 4 x 0.5 mm). The targeted gases were low concentrations of three volatile organic compounds (VOCs): octane, toluene and propanal. The polymer type and thickness and so as the test gas nature have a great influence on the sensitivity and selectivity of this sensor type.

Wanekaya et al. (2005) have fabricated and tested a multiarray polymer sensor by integrating the sensor array with a gas chromatograph. They also compared the performance of the system with a contemporary thermoconductivity detector for the identification and detection of different volatile organic compounds (VOCs). These sensor arrays were not only able to detect the different compounds but also demonstrated a very wide linear response to the amounts of VOCs exposure.

2.10.3 Carbon Nanotubes

In this paper, Li et al. (2006) describe the production of MWNTs produced by a CVD method, using a semi-automatic rotating procedure. Li et al. then investigated the tensile properties and NH_3 sensing behavior of the material within 50-1000 ppm. Using same method to produce MWNTs, Ionescu et al. (2006) reported the responsiveness of MWNTs in gas sensing. The material produced put on the plasma treatment. After that the MWNTs were put on the substrate which can be seen in the Fig. 2.14. The results exhibit relatively sensitive to NO_2 and NH_3 in ppb scale.

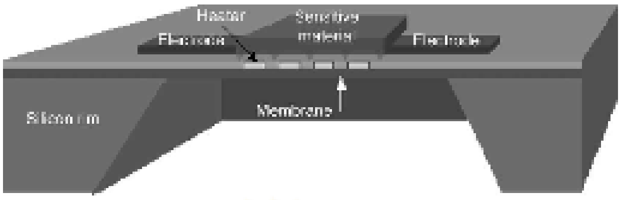


Figure 2. 14 An electrode from silicon (Ionescu et al., 2006).

Lucci et al. (2005) demonstrated efficient NH_3 detection in single wall carbon nanotubes (SWNT) ordered by mean of dielectrophoretical process. Their approach was to disperse the nanotubes in $CHCl_3$ and distributed the suspension between the tracks of multifinger Au electrodes on SiO_2/Si substrates. The NH_3 concentration as targeted gas was detected in range of 100-800 ppm. With similar method, Lucci et al. (2006) reported detection results on NOx. The sensitivity measurement conducted by using gate voltage as operated at different temperature. As a result, the sensor material enable detect up to 2 ppm of NO_2 concentration.

In this paper Parikh et al. (2006) described the fabrication and performance characteristics of a robust and flexible vapor sensor based on films of SWNT bundles deposited directly from aqueous surfactant supported dispersions on plastic substrates, see Fig. 2.15. Two composite were prepared to make comparison SWNT/PET and CB/PET composite. It seems that first composite more sensitive when the composite exposed to toluene vapor. The substrate was used can be seen in the figure below.

Figure 2. 15 Sensor material coated onto a plastic (Parikh et al. 2006).

Quang et al. (2006) in their study reports the effects of temperature and NH_3 adsorption on the electrical properties of SWNT bundles. A certain mount of SWNT dispersed in terpenieol $C_{10}H_{17}OH$. The sensitivity measurement was applied to NH_3 within 0-60 ppm and temperature up to 350^oC. They concluded that SWNT cmight be semiconductive below 100^oC and transform to metallic over than 100^oC.

In the present study, Suehiro et al. (2006) explored the possibility of electrokinetic manipulation of singlewalled carbon nanohorns (SWNHs). The SWNHs differs from CNTs. Hence the author makes comparison SWNT, MWNTs, and SWNHs. All nanoparticles were dispersed in ethanol then ultrasonication for 60 minutes. The pasty from this solution deposited onto glass substrate using photolithography method. The sensor material exhibits good sensitivity in range 10 ppm of NH_3 and NO_2 gasses.

In this work, the authors perform a combined experimental and theoretical study on CNT-based systems for gas sensing applications. In particular, Valentini et al. (2004a) used aligned nanotubes which deposited onto Si_3N_4/Si substrate patterned with platinum by pulsed plasma enhanced chemical vapor deposition (PECVD). The measurement of sensitivity exhibits sensor material has good response to NO_2 in low concentration. Next work Valentini et al. (2004b) reports the electrical response of carbon nanotubes (CNTs) thin films to NO_2, CO, NH_3, H_2O and C_2H_5OH. The sensor material was grown on Si_3N_4/Si substrate using radiofrequency plasma enhanced chemical vapour deposition (r.f. PECVD) method. The electrical response has been measured exposing the films to the interfering gases at different operating temperatures between 25 and 250^{o}C. Upon exposure to NO_2 (10–100 parts-per-billion (ppb)) the electrical resistance of CNTs is found to decrease. The exposing to water vapor exhibits as well as NO_2. Onto similar substrate, Nguyen et al. (2007) reported that the CNTs growth was achieved by decomposition of acetylene (C_2H_2) on sputtered Ni catalyst nanoparticles surfaces on Si wafer. The resistance measurement of the gas sensor based-CNTs was carried out at room temperature with various gas concentrations by the current–voltage technique.

In this report, Paez et al. (2004) demonstrated that films of aligned CNx nanotubes as shown in Fig. 2.16 could act as fast responsive sensors. The authors synthesized CNTs using thermo-lyzing benzylamine ($PhCH_2NH_2$) and ferrocene as catalyst. Two forms of sensor fabricated. First type is compress pellet and second films of aligned CNx nanotubes. Each sensor put inside a sealed pyrex container then chemical vapor flowed in regulated by mass flow controller.

Figure 2. 16 Carbon nanotubes compressed as sensor material (Paez et al., 2006).

2.10.4 Semiconductor and Carbon

In order to investigate the feasibility of combining the gas sensing characteristics of CNTs and WO_3 films, Bittencourt et al. (2006) used combination of CNTs and WO_3. The Si_3N_4/Si substrate was used in the author's work. There were three type sensor material prepared. Of the three materials, hybrids films with content slight of MWNTs exhibit good response to NO_2, NH_3, and CO. Similar method conducted by Cho et al. (2006) and represented their work growing vertical MWNTs on a thin cobalt catalyst layer patterned by conventional photolithography between two parallel patterned electrodes. As substrate was Si wafer. Onto the Si wafer SiO_2 was thermally grown followed by Si_3N_4. Finally the MWNTs with cobalt catalyst was grown using CVD method.

Valentini et al. (2004c) reported results obtained for self-assembled CNT thin films prepared by pulsed radiofrequency plasma enhanced chemical vapor deposition (PECVD) glow discharge investigating the influence of oxygen exposure on the CNTs' sensitivity to CH_4 gas at room temperature. Then they discussed the important effect of both structural defects and oxygen vapor on the carbon nanotubes conductivity.

Wei et al (2004) reported the fabrication involved heat-treating the SWNTs/SnO_2 layer, which was fabricated by spin coating using an organometallic solution of dispersed with SWNTs. The hybrid sensor is utilized to detect NO_2 concentrations in flowing air or N_2, by considering alterations in electrical properties. The tests using an electrode as shown in Fig. 2.17 are performed at room temperature. With different method Liu et al. (2006) reported that a compound material of multi-walled carbon nanotubes (MWNTs) coated with SnO_2 could be used as sensor candidate. In their method, MWNTs were produced by the catalytic pyrolysis of methane on Ni catalyst at 450 ^{o}C. The MWNTs then dispersed in solution comprised of $SnCl_2$, H_2O, and HCl. To make pasty the solution dispersed in terpineol then the pasty deposited onto alumina substrate. The ethanol vapor and LPG were used as targeted of sensor material.

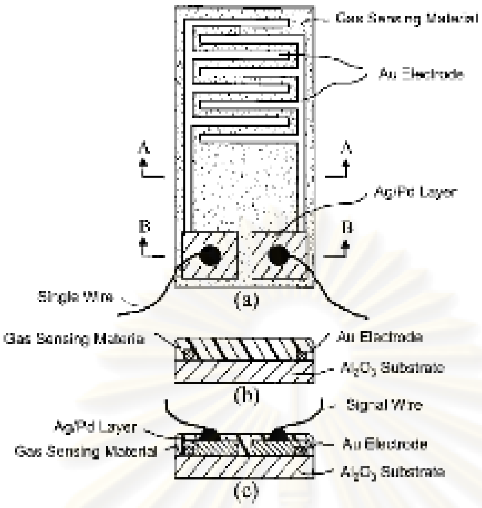


Figure 2. 17 An electrode from ceramic with interdigitated lines (Wei et al., 2006).

In their paper, Hieu et al. (2008) presented their research on gas-sensing properties of SnO_2/MWNT composites. The objective of the author was to take advantage of both SnO_2 and CNTs to develop room temperature gas sensors to detect NH_3 gas. The commercial MWNTs with different diameter and cetyltrimethyl ammonium bromide were added and dispersed in the SnO2 dispersion by ultrasonic vibration for about 1 h to obtain a wellmixed suspension. The sensor material was deposited onto hotplate substrate then put inside a glass chamber. The results of exposing to NH_3 exhibit much better response and shorter response-recovery time, compared to those of the sensors based on the SnO_2 or CNTs material alone.

Chen et al. (2000) studied the morphology and gas sensitive properties of composite films. Graphite and carbon-black particles are dispersed in a silicone rubber solution respectively. The dispersion was printed on ceramic substrates with evaporated Al electrodes and then vulcanized and dried at specific temperature. The results show response speed of sensor is related to morphology of composite films.

2.10.5 Tungsten and Tungsten Oxide

Molecularly tungsten (W) has a structure so called as body-centered cubic which can be seen in Fig 2.18.

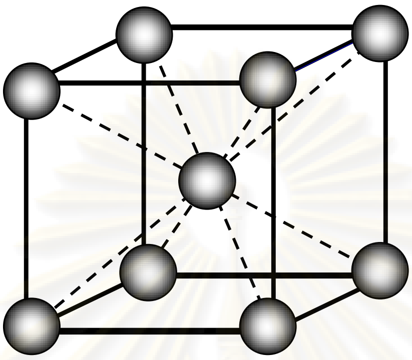
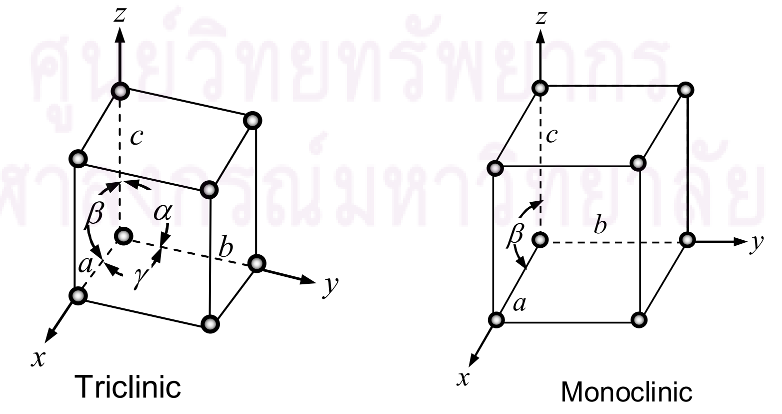


Figure 2. 18 One of three crystal structures, body-centered cubic**.**

Besides some of the crystal structure consists of monoclinic and triclinic system as can be seen in Fig 2.19 with typical pattern of X-ray diffraction as shown in Fig 2.20 (Smith and J. Hashemi, 2006). The numbers above the peaks in Fig 2.20 indicate the lattice points.



Triclinic

$\alpha \neq \beta \neq \gamma, a \neq b \neq c$

Monoclinic

$\alpha = \beta = 90^{o}\ (\neq \beta\ ; a \neq b \neq c\ )$

Figure 2. 19 Triclinic and monoclinic structure.

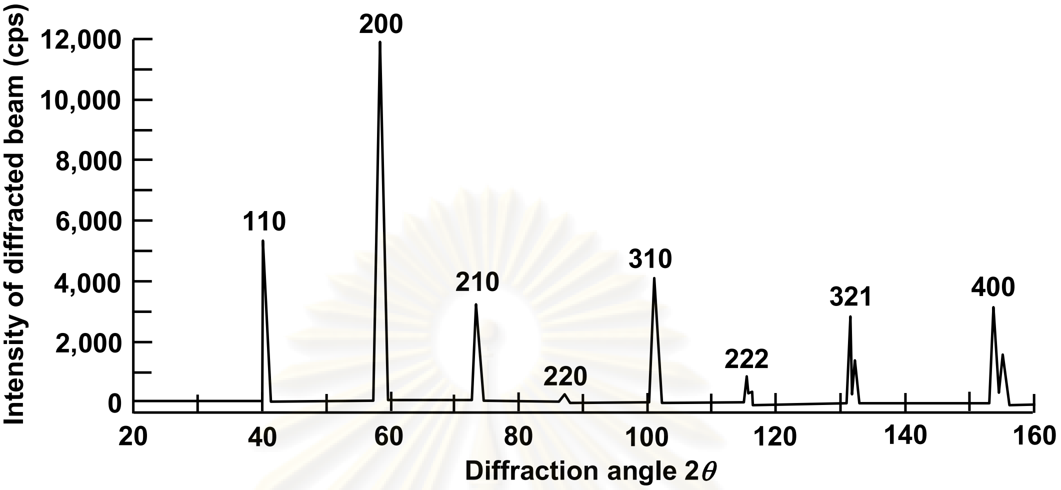


Figure 2. 20 X-ray diffraction for tungsten.

Although pure tungsten has high melting point, 3422°C, tungsten in oxide form i.e. tungsten oxide (WO_3) has low melting point, 1473°C (Wikipedia.org). Typically, the X-ray diffraction (XRD) pattern of WO_3 could be showed in Fig. 2.21. The detailed discussion about the peaks related to tungsten oxide can be referred to International JCPDS database. In the database one can interpret the peaks shown by X-ray diffraction (Sibuyi, 2006).

The using of WO_3 as sensor material has been acknowledged (Papadopoulos et al., 1996). Several factors should be considered when employing tungsten oxide as sensor material such as thickness, dopant type, doping method, deposition temperature, annealing procedure and operating temperature (Marquis and Vetelino, 2001). Those factors influence the sensitivity of WO_3 ad sensor material.

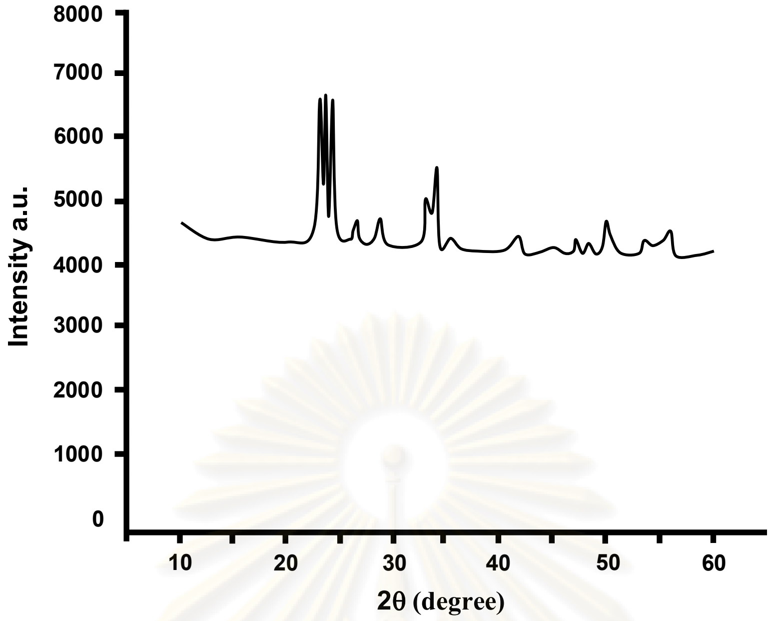


Figure 2. 21 X-ray diffraction for tungsten oxide (Nimittrakoolchai and Suppotina, 2008).

Experimentally there are several methods to get tungsten oxide. Among methods are arch and discharge vaporization of tungsten metal (Solis et al., 2001), sol-gel (Galastis et al., 2001) precursor mixing (Tanaka et al., 2004), precipitation (Supothina et al., 2006, Balazsi et al., 2008).

Based on many reports it is known that tungsten oxide and its composite sensitive to certain gasses. Marquis et al. and Balazi et al. report that NO and NH_3 easily detected by WO_3. Besides, H_2S (Solis et al., 2008), NO_2 (Jin et al., 2005), O_2, CO, (Galastis et al, 2001) are gasses which also could be detected.

To take benefit of WO_3 characteristics, some composite materials incorporated with polymer has been developed and investigated (Parvatikar et al., 2006, Patil et al., 2008, Bittencourt et al., 2006).

CHAPTER III

EXPERIMENTAL

In this chapter how to synthesize, characterize, and measure response of sensor materials will be discussed.

3.1 Carbon Nanotubes and Chemicals

a. **MWCNTs**. Around ten years ago the price of CNTs per gram was very high. In line with time the price is going to be low. The decreasing of the price might caused by many institutions or research center can synthesize carbon nanotubes they self. It is known that at least the CNTs can be synthesized through three methods (Lau and Hui, 2002) such as arch discharge, chemical vapor deposition (CVD), or laser ablation. In CEPT laboratory, MWNTs can be synthesized using pyrolysis or arc discharge method. To get much of information related to involving of MWNTs in composite it is required a lot of MWNTs. The material could be used to observe its surface or to employ in polymer matrix. Since limitation time the use of MWNT- synthesized in lab-scale is not possible. Purification and characterization leads the use of MWNTs-synthesized need so much of efforts. Therefore employing of commercial of MWNTs could be effectively. Fortunately, the commercial of MWNTs produced by Bayer Co. could be procured from NANOTEC trough Aj. Apinan.

   Fig. 3.1 shows the micrograph of MWNTs used in this work. Fig. 3.2 shows the XRD pattern of MWNTs of Bayer Co. The peak occurs within 2θ angle in range of 20-30^o explaining MWNTs.

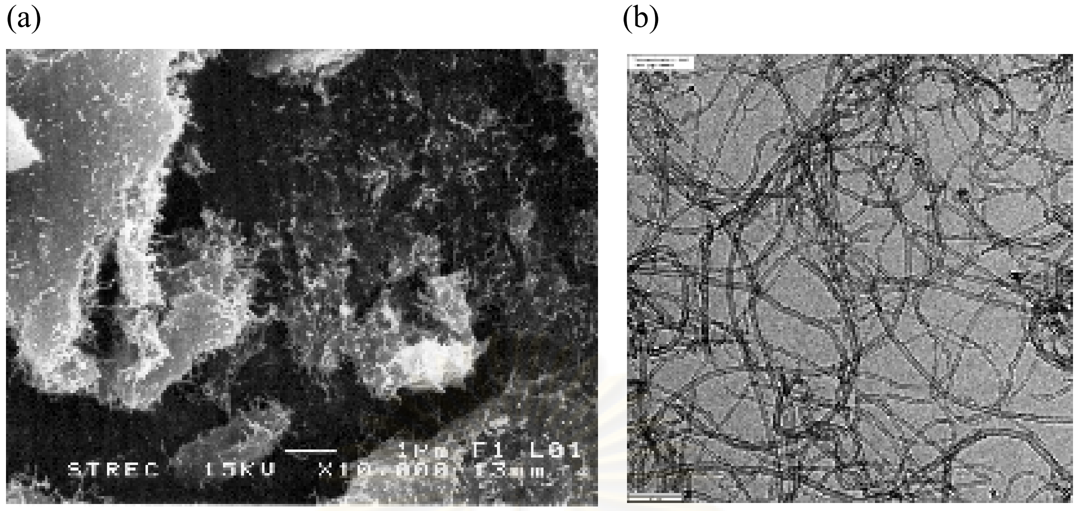


Figure 3. 1 Micrographics of MWNTs of Bayer Co. (a) SEM, (b) TEM.

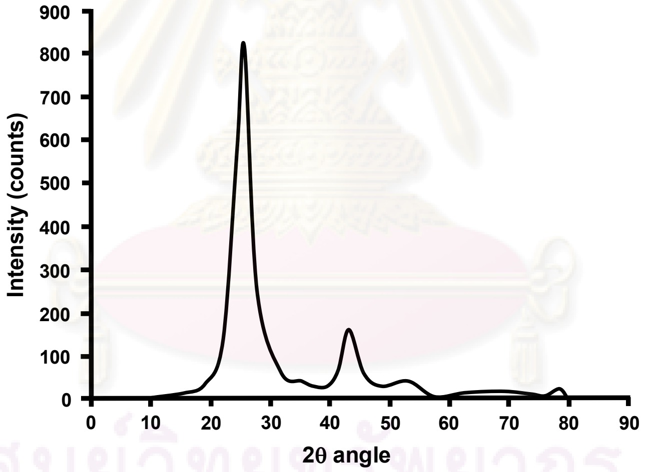


Figure 3. 2 X-ray diffraction of MWNTs of Bayer Co.

b. **Poly(p-phenylene)** (PPP) This material is not available commercially. The polymer must be synthesized using the procedure as reported by (Kunanuruksapong and Sirivat, 2007).

c. **Benzene (C_6H_6)** Benzene is a monomer to produce PPP purchased from Panreac, Spain.

d. **Cupric Chloride ($CuCl_2$)** and **Aluminum Chloride (Al_2O_3)** are catalyst bought from Riedel de Haen, Germany.

e. **Ammonium tungstate parapentahydrate** (ATP), $(NH_4)_{10}W_{12}O_4.15H_2O$ purchased from Wakao was used as precursor for tungsten oxide.

f. **Nitrogen** purchased from Thailand Industry Gas (TIG)

g. **Sensing gas** Chemical vapors used as sensing gas are alcohols, toluene, benzene etc.

3.2 Apparatus

Apparatus required in the experiment consists of

a. A three neck glass
b. A water bath
c. A separation funnel
d. Electric stoves
e. Thermometers
f. pH indicators
g. Beaker glasses
h. A glass chamber with 500 mL
i. A microbalance

3.3 Synthesizing Procedures

3.3.1 Synthesizing of Poly(p-phenylene)

The synthesizing of poly(*p*-phenylene) (PPP) was carried out based on a report written by Kunarunuksapong and Sirivat (2007). The procedures are following.

Amount of benzene, $AlCl_3$, and $CuCl_2$ with certain ratio were dropt into a three-neck flask. Temperature in the flask was kept around 35-37°C using a water bath. The reactant and catalysts were kept for 2-3 h as the schematic of synthesizing system shown in Fig. 3.3. After a period of time the black-solid product removed from reactor then cooled to 5 °C.

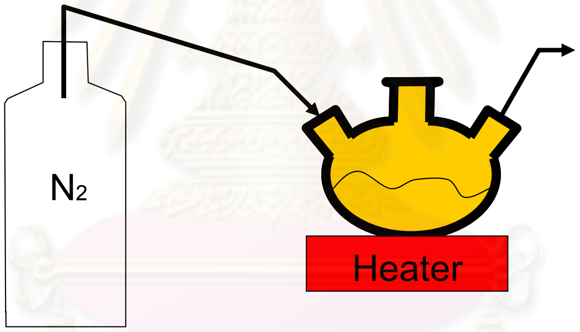


Figure 3. 3 Schematic of PPP synthesizing**.**

The black-solid product then washed by 18% HCl solution. Up to this step the color of product slowly changed to brown-powder. After that, the brown-powder (PPP) was washed with boiling 18% HCl solutions until the washing solution was colorless. The poly(*p*-phenylene) powder was finally washed with hot water until the washings had a pH of 7. The pH papers used to make sure the solution is not acidy. The poly(*p*-phenylene) was filtered out by a funnel and the final product can be seen in Fig. 3.4.

Figure 3. 4 Appearance of polymer poly(p-pheny-lene) produced.

3.3.2 Synthesizing of Tungsten Oxide

Production of tungsten was conducted by three methods. First method precursor without pretreatment was put as shown in Fig. 3.5. Second method, precursor- pretreated was sintered without glycerol and ferocene then the material were placed as shown Fig. 3.5. Third method, similar to second method but sintered with glycerol and ferocene.

A furnace with quartz tube has been used for sintering the ATP. The schematic of the furnace described in Fig. 3.5.

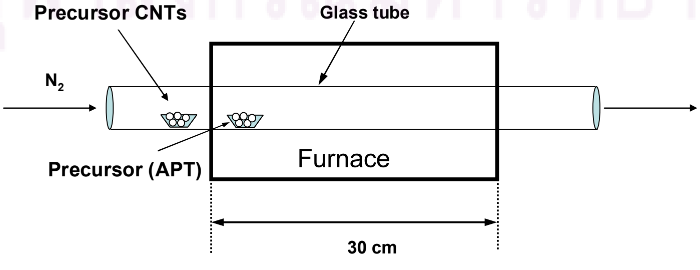


Figure 3. 5 Schematic of the furnace for sintering tungtate oxide.

Before sintering the temperature profile has been measured. Fig 3.6 shows the temperature profile around the furnace.

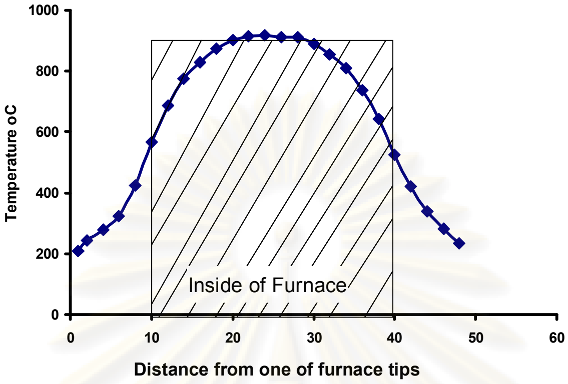


Figure 3. 6 Temperature profile inside of the tube.

Pretreatment procedure was conducted as follow. In a small vial amount of one gram ATP mixed with one milliliter of HCl 37%. The solution then sonicated within 30 minutes. After that the vial put in an oven to vaporize the acid. In this case we used temperature 150 ^{o}C within 20 minutes. The product was solid with yellow color. A part of product was separated and put in a small pot then put inside the furnace as shown in Fig 3.5.

Carbon nanotubes (CNTs) to be composed with tungsten oxide were coming from pyrolysis method. The procedure of synthesizing is firstly lying on ATP boat inside quartz tube as shown Fig 3.5. Then temperature at middle of furnace was set 900^{o}C and nitrogen flow in the tube with 175 mL/min. Therefore the temperature at the boat position was 740^{o}C. When temperature was stable within 1 h, the mixture consists of glycerol and ferocene as catalyst with mole ratio 10:1 put in quartz tube as shown in Fig 3.5. After a night the products were taken out.

3.3.4 Characterization and Measurement

a. To confirm of PPP the characterization of polymer was conducted using FTIR with model PerkinElmer.
b. The observation on surface of sensing film was conducted using SEM.
c. Bruker AXS D8 Discover X-ray diffractometer (XRD) was employed to observe the structural of WO_3.
d. Thermo gravimetric analysis (TGA) was conducted using Mettler Toledo, TS0801 RO TGA/SDTA851 with temperature rate of 20^oC/min.

3.5 Sensing Measurement

3.5.1 Fabrication of Sensor Material

MWNTs, PPP, and terpineol (Quang et al., 2006) were mixed in a small vial then sonicated for certain period. The ratio of MWNTs and PPP was varying likewise amount of terpineol. Besides, in certain case time for mixing was considered. Fig. 3.7 shows the mixture in a small vial under ultrasonic probe. This procedure was also conducted to fabricate sensor material from WO_3.

Figure 3. 7 The solution under the sonication probe**.**

3.5.2 Coating the Sensor Material onto the Electrode

At least there are three kind of substrate for fabrication sensor. The researchers used silicon as substrate to fabricate the sensor (Ma et al., 2006), (Valentini et al., 2004). Another researcher used plastic (Lucci et al., 2005), (Valentini et al., 2004), (Chen et al., 2005) And other used glass (Arshak and Gaidan., 2006), (Merkoci et al., 2005). In this study we used plastic as the substrate.

In this experiment the substrate was made from printed circuit board (PCB) plastic, see Fig 3.8. The solution got from previous step then coated onto electrodes. The electrode is a rectangular form. Onto the substrate there are two metal strips with distance one millimeter apart. The pasty coated manually in the gap between the metal strips, see in Fig. 3.8 and 3.9. After that the electrode with the sensor material coated put into an oven at 75^{o}C for several hours. Every hour the resistance of the sensor material was checked using digital multimeter. When the resistance constant the electrode put in a desiccator to avoid contaminated by environmental. The two metal strips then connected to the measurement system. The electrode then lay in a glass chamber in which gas sensing will be exposed.

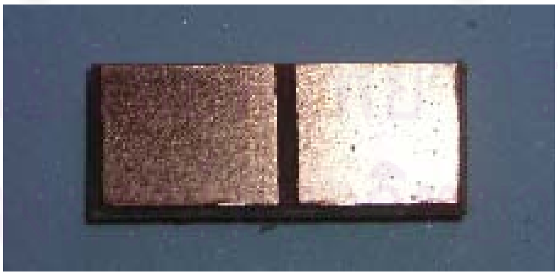


Figure 3. 8 The real electrode before coating.

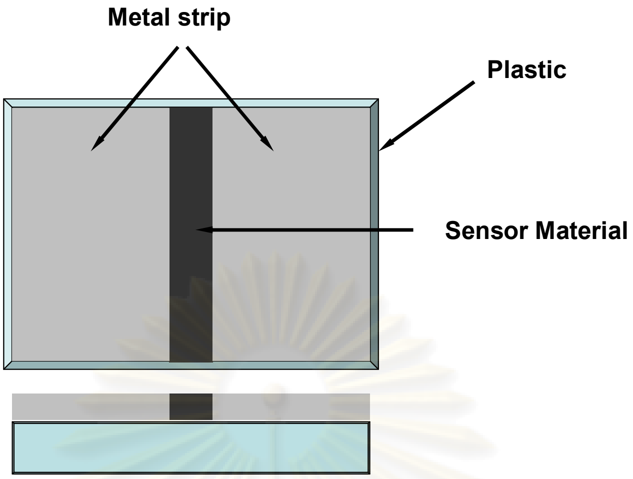


Figure 3. 9 Schematic of an electrode, (a) top view, (b) cross section view.

3.5.3 Data Recorder

To measure the sensitivity of material fabricated, first of all the electrode was mounted on system measurement as depicted in Fig. 3.10. Before exposed to chemical vapors the electrode put in an Erlenmeyer to reduce disturbances from environmental. After that, the heater underneath of glass chamber then turned-on until temperature at the bottom of chamber 70-80 ^{o}C. This will cause the temperature inside the chamber around 40 ^{o}C. Amount of chemical was injected to the chamber then waited a view minutes in order all chemical vaporized. Finally the electrode was inserted immediately into the glass chamber. Within certain time interval the electrode was pull out then inserted again periodically.

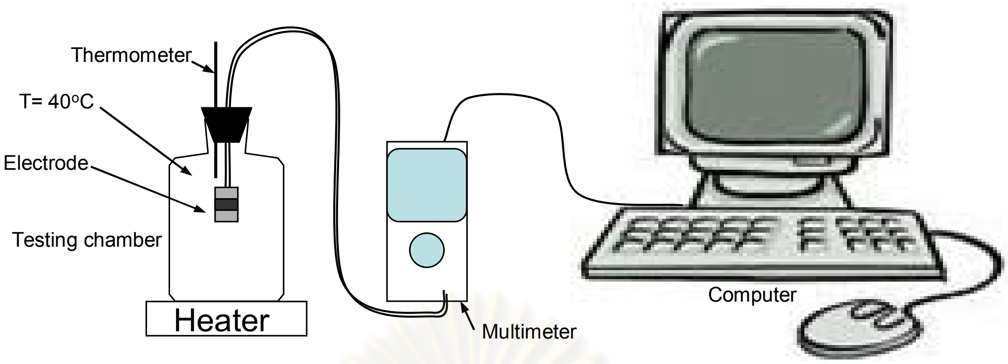


Figure 3. 10 The measurement system for sensing analytes.

The responses of sensor recorded automatically by a computer connected to sensor. In this case a digital multimeter with model AT-9995, see Fig. 3.11, has connecting system to the personnel computer (PC). Using a software accessory of the digital multimeter the computer records data automatically when the multimeter turned-on. The recorded data may be saved in a file then converted to an excel file.

Figure 3. 11 The digital multimeter used in this work.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter the results of experiment will be presented into several sub chapters. The sub chapters are: influence of MWNTs content on initial resistance, effect of sonication, effect of terpineol content, and response of sensor material to other chemical vapor. The discussion about tungsten oxide is put at the final part.

4.1 Influence of MWNTs Content on Resistance of MWNT/PPP Composite

Basically every material has its own electrical resistance. Data of the resistance can be seen in many handbooks. The magnitude of resistance of a material depends on the molecules configuration of the material. It has been known that if a material has molecular structure like metal its electrical resistance tends to be low.

Due to a certain objective, electrical resistance of materials can be modified. The modification can increase or decrease the resistance of a material. The simple way to modify resistance of a material is by mixing the material with another material which has different resistance. Another way is applying chemicals which are called dopant. The addition of dopants to a material will produce a material with new electrical properties.

To use a material as a gas sensor, a material must have a specific resistance. In short, the material should have measurable resistance. When the material cannot be identified its resistance, it is difficult to utilize the material as sensor. In fact, the fluctuation of resistance or conductivity plays main role in sensor system.

Generally a polymer is an insulator which has relatively high resistance. However, around two decades ago it has been discovered a new kind of polymer which is conductive. The discovering has been a mile stone for development application of polymers in electronic. Nowadays it is known that the conductive polymer normally have double ring in its structure.

If we see from the structure of polymer, PPP has double ring in its structure. That means the polymer is potential to be conductive. By involving a dopant such as arsenic fluoride (AsF_5) the resistance of PPP will decrease. Due to AsF_5 is very toxic and harmful it is unreasonable to employ the dopant. However, the involving of MWNTs into PPP can also decrease the resistance of the polymer. In this case the MWNTs become a reinforcing phase of PPP matrix.

MWNTs is an allotrope of carbon. This material was popularized by Iijima almost twenty years ago. Both of single carbon nanotubes (SWNTs) and MWNTs have been used as sensor material. As single component, however, the CNTs can only be used for sensing certain gasses or chemical vapors. If we want to utilize the tremendous property of the CNTs to various gasses we must employ it with other material. In this moment it seems the MWNTs favor to be involved with PPP to get sensor composite.

The using of an allotrope carbon as additional material to polymers is not new news. Many researchers have reported involving allotropes carbon, especially carbon black (CB), to get a specific mechanical property of polymer. Besides, the carbon black has also been used as a part of sensor material with polymers. As a result the performance of polymer composite shows favor results.

What has been achieved by CB/polymer composite is an appreciated work. Since carbon nanoparticles (CNP) have a unique property both electrical and mechanical, scientists devote their efforts to investigate CNP composite for several applications. Wang et al. (2007) has discussed the using of fullerene, C_{60} in polymer to be applied in photoconductivity, photorefractivity, photovoltaic cell, and optic liming.

In our experiment, before use MWNT/PPP as sensor material we investigate the influence of content percentage of MWNTs. The measurement of resistance with different content of MWNTs is presented in Fig. 4.1**.**

As shown in the figure when PPP without MWNTs the resistance of the polymer could not be detected by our digital multimeter. By involving 5 wt.% of MWNTs the resistance of composite measured within two thousands kΩ. It might be deduced that the threshold of electrical resistance occurs between 0-5 wt.% of MWNTs. The content of 20-25 wt.% leaves the resistance of composite tend to be constant. In the figure, addition up to 10 wt.% exhibits changing of resistance dramatically. These results has similar trend with other report using different material. It is reported by Kymakis et al. (2002) that the mixing of poly(3-octylthiophene) (PO_3T) and more than 12 wt.% of SWNT exerts the conductivity of polymer increase. As the fraction of SWNT increases further, the average distance between the nanotubes becomes sufficiently small for the electron to tunnel through the polymer or for many physical contacts between nanotubes to be formed. When the SWNT less than 12% the polymer isolates the nanotubes and controls the property of composite. Besides its conductivity, the dielectric constant of composite would change when some MWNTs employed to the composite (Liang et al., 2006). Whereas, Zhang et al. (2005) reported that addition of 1-10 wt.% MWNTs into polystyrene reduced the resistance of the polymer up to 10^6. Similarly, poly(methyl methacrylate) (PMMA) which added by 1 wt.% of MWNTs reduced the resistivity of polymer up to 10^9 compared to the virgin polymer. With addition 4.7 wt.% of MWNTs the resistivity of PMMA decreases not significantly (Yuen et al., 2008). Likewise, Zhu et al. (2006) reported that the conductivity of polyimide increases when 7-10 wt.% of MWNTs were added into the polymer. The involving of more MWNTs leads creating more conductive paths.

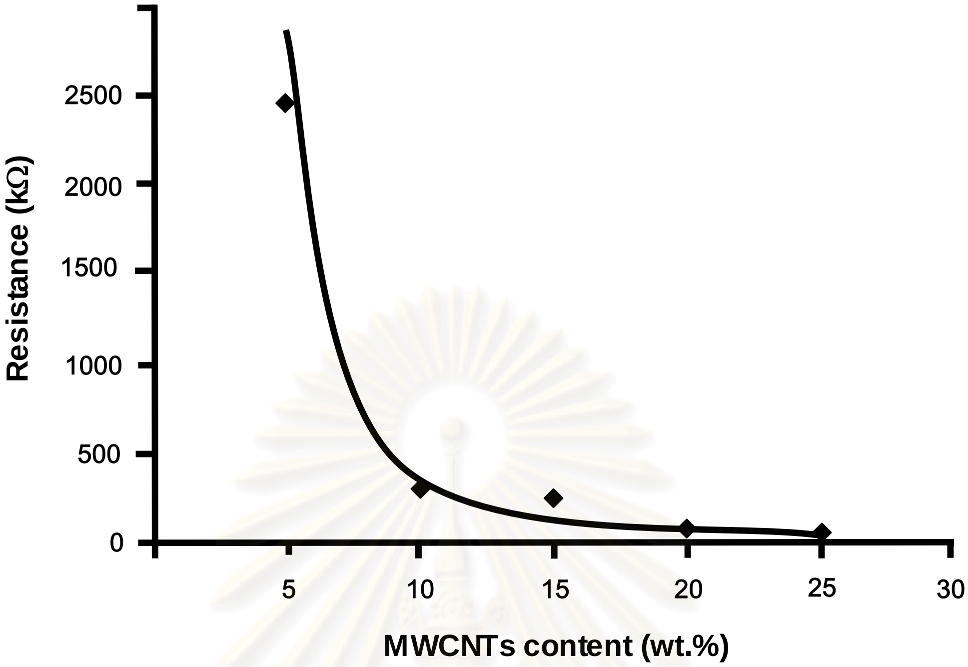
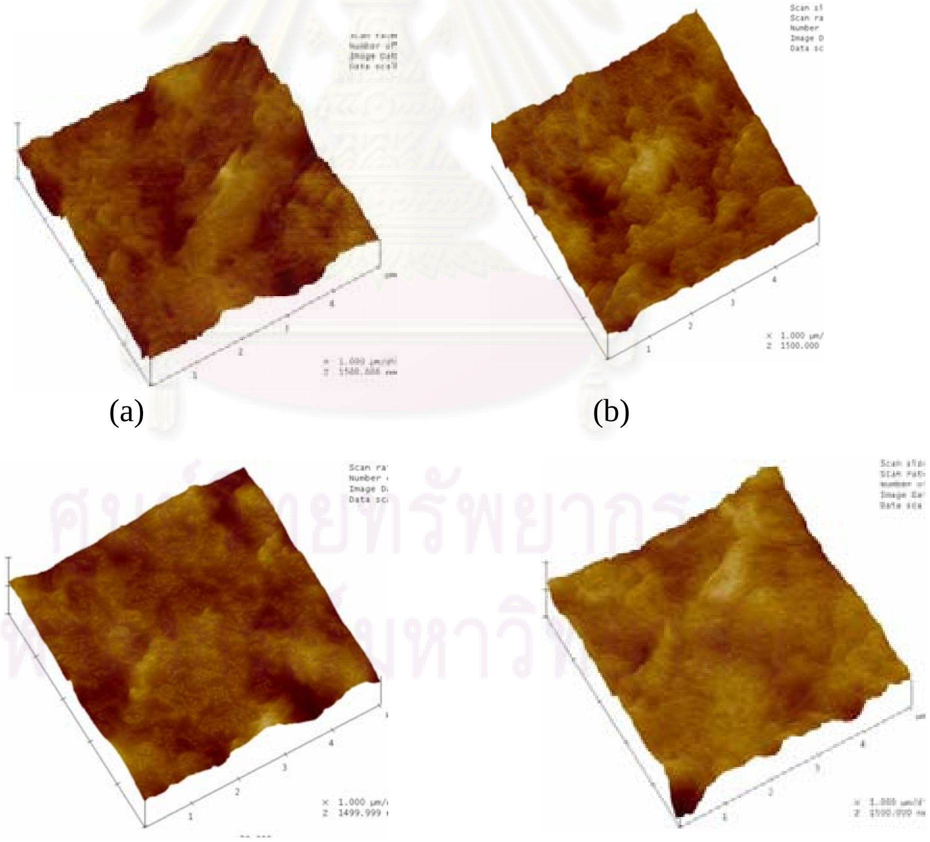


Figure 4. 1 Initial resistance of composites in various contents of MWNTs**.**

Generally, the bonding between MWNTs and PPP occurs through van der Waals interaction (Li et al., 2006). Decreasing of resistance of polymers when CNP or CNTs involved inside, is attributed to formatting of conductive bridges for electron transport. The electrons use the bridge to migrate among the chain of polymer. More the MWNTs involved the resistance decreased dramatically. In this case, the helical conformation of the polymer around MWNTs is one key to see the strong bond between MWNTs and polymers. On the surface the strength of the interface may result from molecular-level entanglement of the two phases MWNTs and PPP (Thostenson et al., 2001). As Vaisman et al. (2007) explained that the interaction PPP with MWNTs might occurs through groups in polymer and π bonding system in CNTs. The atomic orbitals of each carbon atom overlap with those of its neighbors to form the π bonding system. This asserted by Wang et al. (2005) that when polymer and MWNTs taking interaction, MWNT/polymer composite involves the π-π electron from CNTs and polymer to create scattering centers in the electrons transport process. However, the mixing of PPP and MWNTs is almost impossible to alter chemical structure of PPP (Zhu et al., 2006).

The observation using scanning probe microscopy (SPM) method reveals that MWNTs play role to determine the character of the surface of composites. Fig. 4.2 represents the SPM images of composite with different content of MWNTs. The content of MWNTs in composites influences the surface of composites. It is shown by Fig. 4.2c-d that more MWNTs added to the composites the smother surface of the composites. More MWNTs involved in composites more interaction between MWNTs with the dispersant. During the mixing the molecules of dispersant surround the particles and might be slightly attached to the particles. The dispersant molecules then hold tighter bonding to form a smooth surface. Apart of the dispersant's molecules removed when the composite put in oven. After heating in oven, however, a part of molecules of the dispersant is still attached around the particles as shown by Fig. 4.3.



(a) (b)

(c) (d)

Figure 4. 2 SPM images of composites at different contents of MWNTs (a) 5 wt.%, (b)15 wt.%, (c) 20 wt.%, (d) 25 wt.%.

Fig. 4.3 shows the TGA analysis of pure PPP and a typical composite, i.e 5 wt.% of MWNTs. Within 670-780°C the weight loss of PPP reduced drastically means at that range of temperature PPP destructed. The chains of PPP are disrupted then atom C and H escape from its structure. This results confirm that the melting point of PPP more than 550°C. The composite curve explains that in the composite there might be a trace of dispersant. The increasing of temperature gives energy for molecules of dispersant to move out from MWNTs or PPP. Perhaps the molecules of dispersant and PPP move out simultaneously.

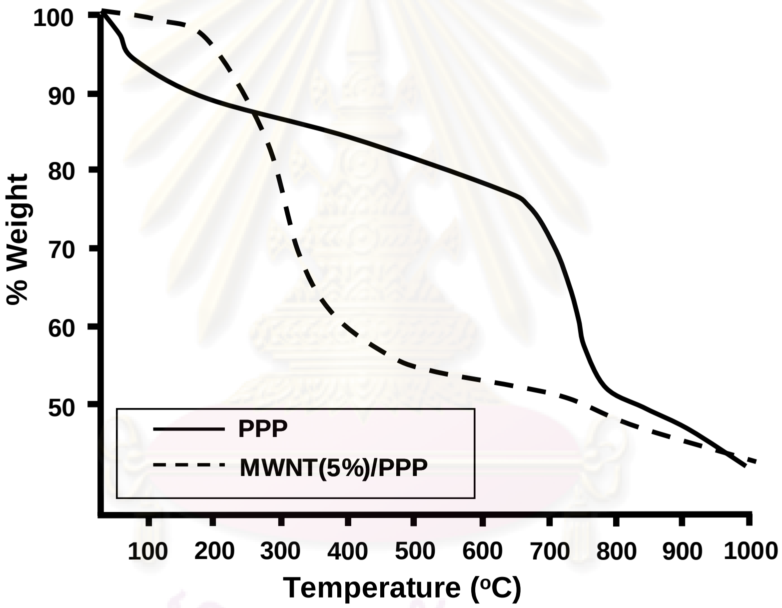


Figure 4. 3 TGA analysis of PPP and composite with 5 wt.% of MWNTs.

4.2 Effect of Sonication

It should be noted that pure PPP has infinitely high electrical resistance. Using the results in Fig. 4.1 then the content of MWNTs employed in the next experiment was 10 wt.%. The fabrication of composites of PPP with a certain amount of MWNTs exhibits electrical resistance in the measurable range of 30–280 kΩ. Results of 10 wt% of MWNTs dispersed in PPP are represented in Fig. 4.4a.

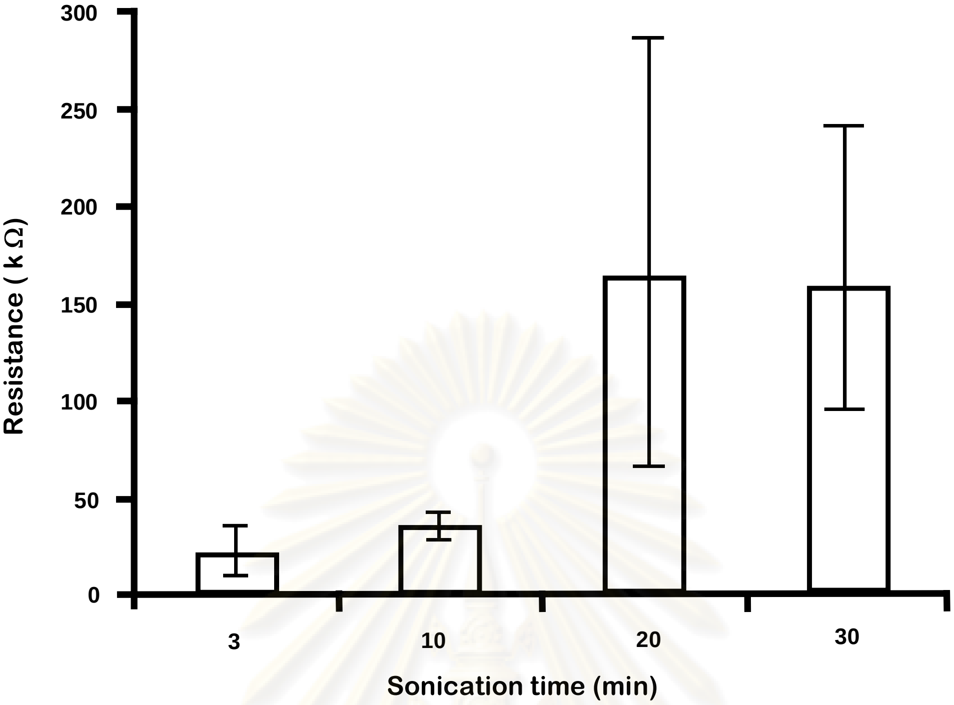


Figure 4.4 a Influence of mixing time on initial resistance of MWNT/PPP composites.

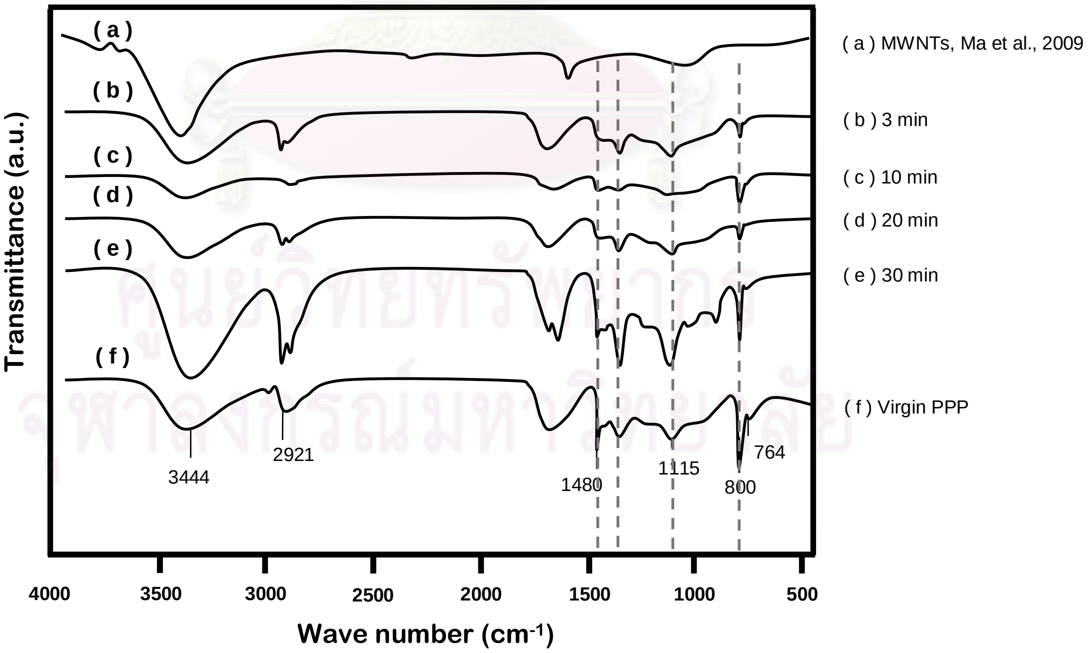


Figure 4.4 b FTIR spectra of MWNT/PPP composites with different mixing time**.**

The involving of MWNTs in terpineol then treated it using ultrasonication is a mechanical method to disperse MWNTs in a solution. Using the method MWNTs are forcedly separated. One effect of the ultrasonication method is decreasing in aspect ratio of CNTs (Vaisman et al., 2006). In addition MWNTs degree of dispersant determined by type of dispersant (Tsai and Huang, 2006). Giving high pressure force in the solution, particles in the solution collide each other. Besides, interaction of MWNTs-dispersant molecules caused by ultrasonic probe has cut MWNTs. It implies that conductivity paths of composite defected. Our experiment results show that time for mixing has a contribution to influence the resistance of a composite as shown by Fig. 4.4a. The mixing time less or over than 10 minutes produces initial resistance larger deviations. The results show that with compounding time of 10 min the electrical resistance of the composite was significantly low and had the narrowest deviation. Three minutes is not enough to MWNTs to distribute homogenously. In contrast, over than 10 minutes it perhaps the MWNTs distribution was not homogenous caused by the agglomerates of the nanoparticles. The agglomeration formed by too long mixing time. The effect of time on CNTs dispersion has also been reported by Yu et al. (2007) and Ryskowska et al. (2007). Based on the reports, the distribution of CNTs in dispersion media would reach optimum within a period of time.

To understand the phenomena during mixing, the FTIR analysis was conducted. Fig. 4.4b shows the results of FTIR of composite fabricated. Based on the FTIR spectra shown in Fig. 4.4b, it was also found that composites with compounding time longer than 10 min would exhibit IR transmittance with the same level. It should be noted that the composite prepared with a compounding time of 30 min would exhibit a different spectrum which would be attributed to segregation of MWNTs from PPP (Chen et al., 2007). These IR spectra reveal that the synthesized polymer has intensive peaks at wave numbers of 764, 800, 1115, 1480 and 2921 cm^{-1}. To understand the peaks shown in the figure the standard table is applied. Referred to IR of PPP, at least there are three ranges of wave length within 700-4000 cm^{-1}. The wave length 700-1000 cm^{-1} explains the aromatic rings, 1000-1500 cm^{-1} means several types of stretching, and 1500-4000 cm^{-1} gives information of functional groups. Based on this range, it is concluded that FTIR result could be read as follows (Palleros, 2000): 3444 and 2921 cm^{-1} are C-H aromatic stretching and aliphatic respectively. The wave length both 1670 and 1480 cm^{-1} are C-C skeletal of aromatic stretching while 764 and 800 cm^{-1} are C-H deformation.

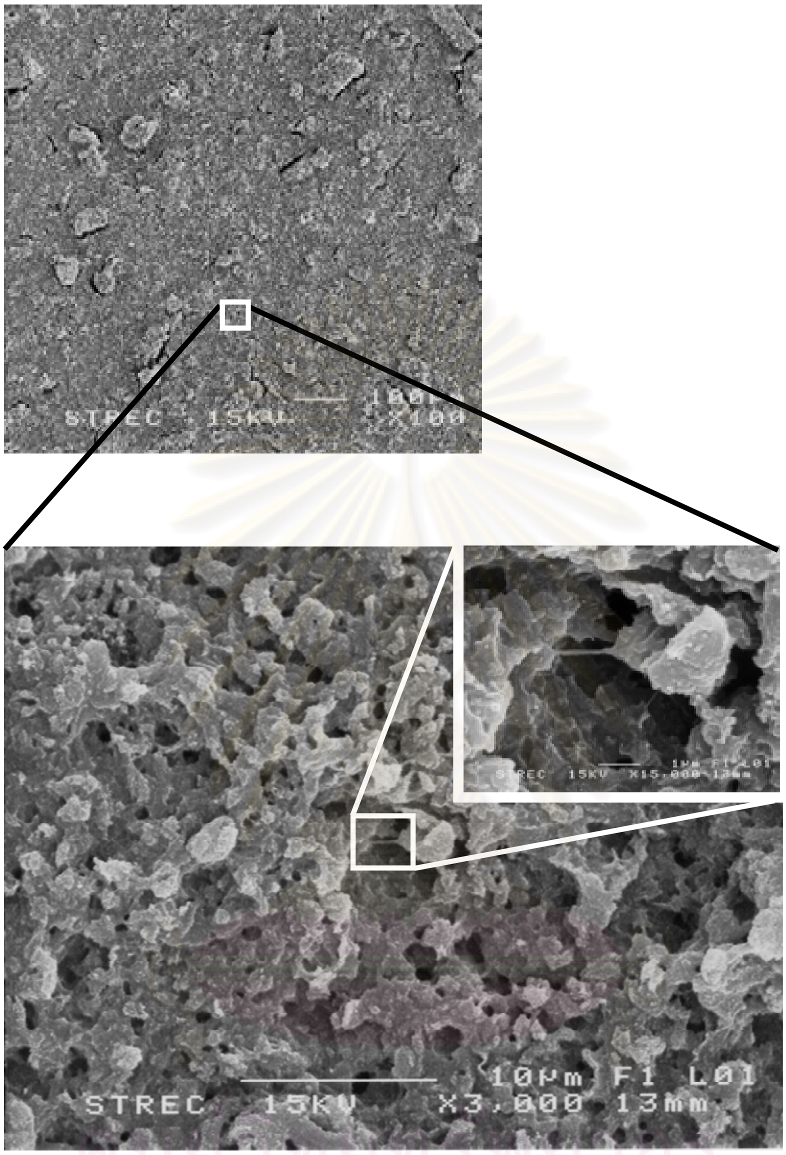
Basically, only based on IR bands such above, we can not determine the structure of polymer exactly. More over it is also difficult to proof that certain peaks has slight change during mixing as shown by Fig. 4.4b and 4.6b. To be more accurate we need to do characterization using Nuclear Magnetic Resonance (NMR) and Molecular Spectrometer (MS). However, as evidence the peaks are similar with results reported by Kunanuruksapong and Sirivat (2007). Therefore we can confirm that the polymer synthesized is poly(p-phenylene). The IR signals occur between 700 and 1000 cm^{-1} implies that phenylene (aromatic) ring was formed. In Fig 4.4b there are two dominant peaks at 800 cm^{-1} and 1480 cm^{-1}. It seems that the two peaks have slight modified when mixed with CNTs and the dispersant.

It should be noted that through comparison of IR transmission between virgin PPP and composites, the IR active phonon mode of MWNT, which could be observed as a peak at 3444 cm^{-1}, gradually increases with compounding time. This evidence indicates that MWNTs could interact with the PPP matrix (Vaisman et al., 2007). As comparison with report of Chen et al. (2007), it is shown that MWNTs slight influence on composite of polypyrrole/MWNTs. Based on the evidences we conclude that the property of MWNT/PPP composite could be modified partly.

Furthermore, microscopic analyses using SEM were also conducted for confirming the tendency of MWNT dispersion in PPP matrix. Fig. 4.5 presents typical SEM images of the composites prepared by different compounding time with the same amount of terpineol. It could be clearly observed that insufficient ultrasonic compounding time (3 min) could not homogenously disperse MWNT in PPP, resulting in the composite with non-uniform surface as shown in Fig. 4.5a. Meanwhile, it should also be noted that heat generated locally by ultrasonication would lead to MWNT/PPP composite with smoother surface (Fig. 4.5b and c). Higher magnification clearly reveals that entangling MWNTs would result in internal connections with conductive paths. However, with the excessive ultrasonication, MWNT/PPP composite would possibly undergo breakage due to thermal stress (Chen et al., 2007). It is reported that during mixing of MWNTs the length was reduced. Gibson et al. explained that reduction of length occurs immediately when mixing started. The reduction after that tends to low (Gibson, 2007)

Also, longer compounding time would result in heat generation to damage the contact between MWNT and polymer matrix (Fig. 4.5d), leading to higher resistance of the composite (Xie et al., 2005). As a result, though the composites obtained at the compounding time of 3 min would exhibit the lowest resistance, based on the physical consistency of the composites prepared with the compounding time in the range of 10–30 min, this time range was intentionally selected for further investigations on electrical characteristics.

(a)


100µm
STREC 15KV X100
1µm F1 L01
STREC 15KV X15,000 13mm
10µm F1 L01
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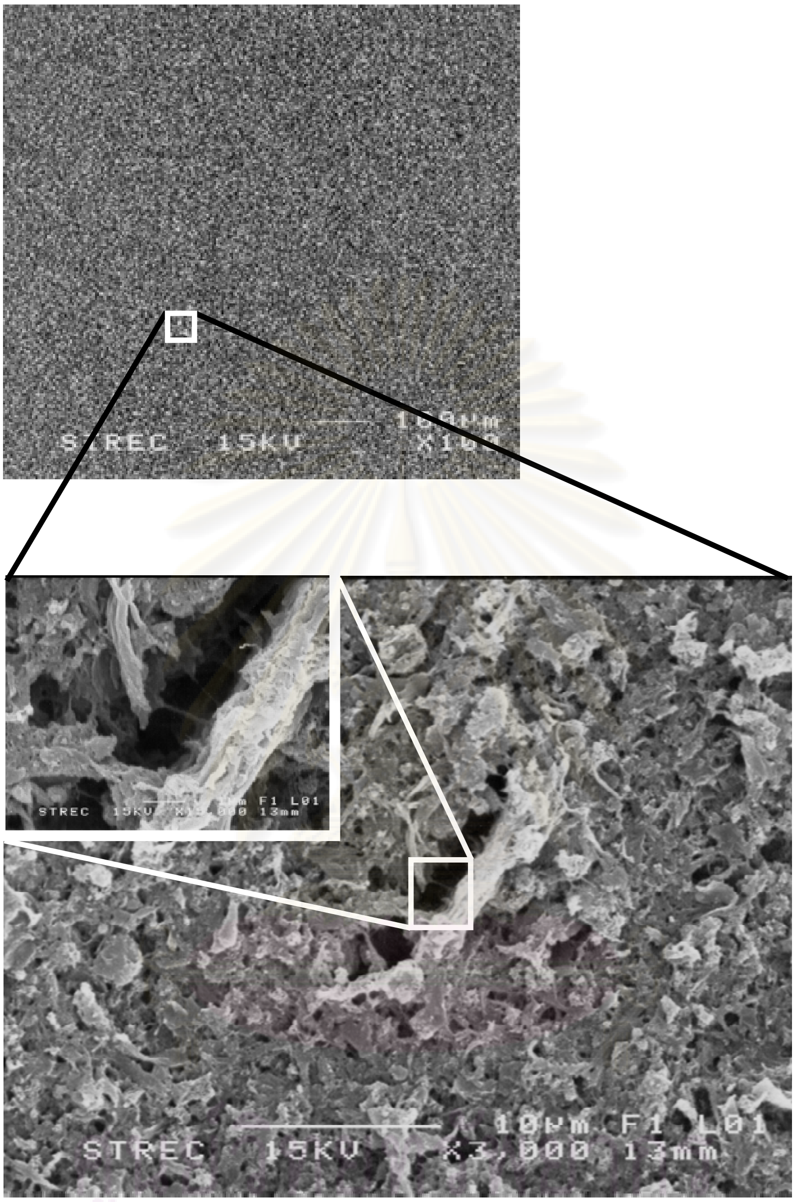
(b)


100μm
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F1 L01
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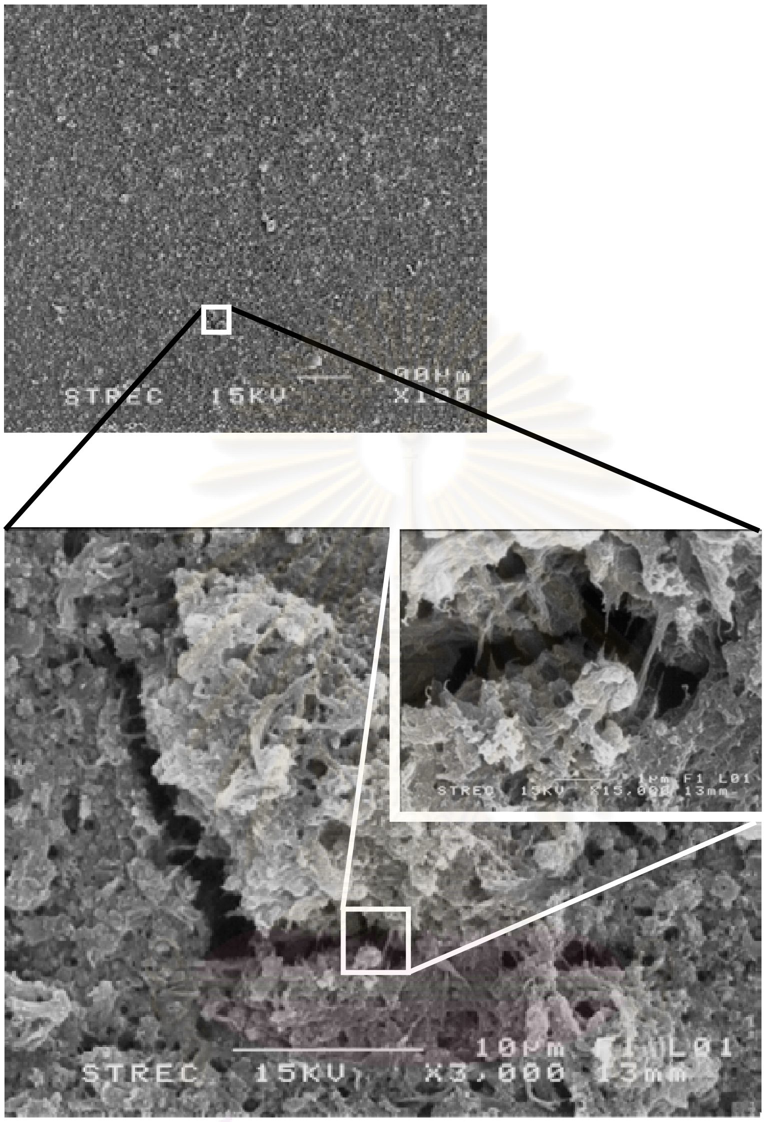
(c)


100μm
STREC 15KV X100
1μm F1 L01
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10μm F1 L01
STREC 15KV X3,000 13mm

(d)

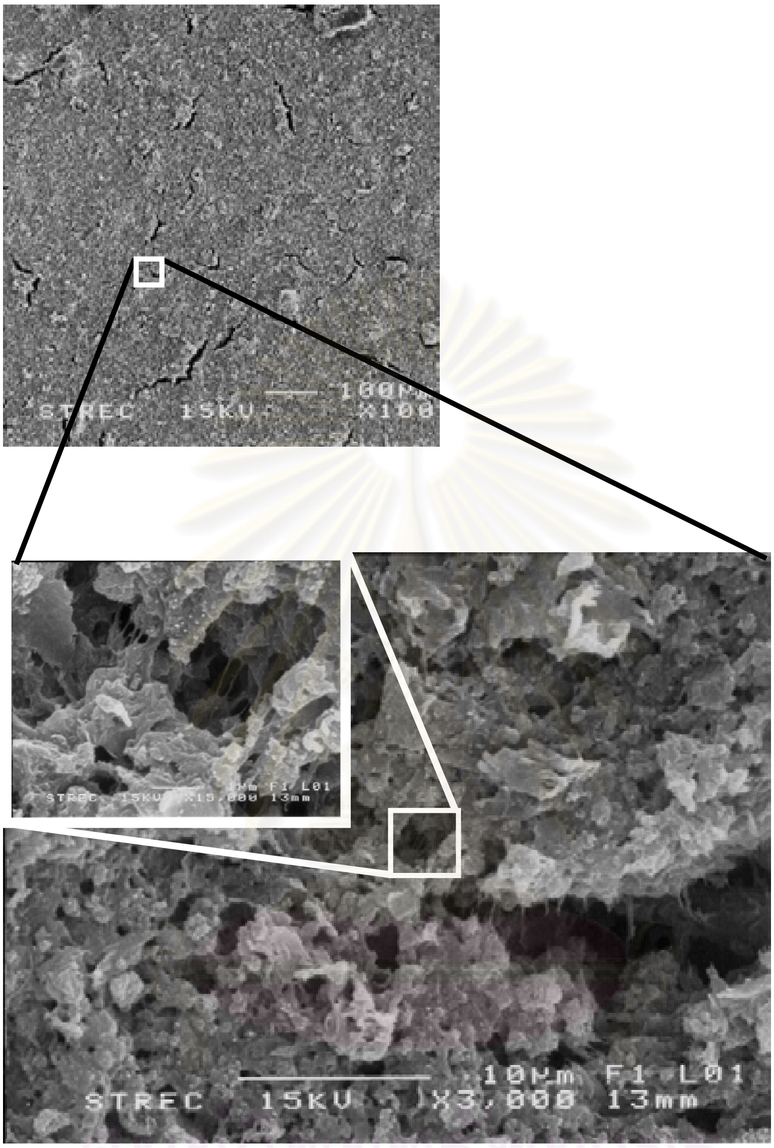


Figure 4. 5 Comparison of composites prepared with different ultrasonicated mixing time (a) 3 min, (b) 10 min, (c) 20 min and (d) 30 min.

4.3 Effect of Terpineol Content

The ratio of dispersant to CNTs influences the interaction of CNTs in the media. As reported by Rastogi et al. (2008) the different ratio results different flocculation form occurring in the dispersant leading different morphology of surface observed. Fig. 4.6a reveals that with increasing the amount of terpineol to more than 2 mL given a certain compounding time of 10 min, the electrical resistance of composites increased significantly, though, with 1.5 mL terpineol an increase in the resistance was also observed. This result is attributed to the reason that excessive amount of terpineol would hinder the interaction between MWNTs and PPP. Meanwhile, low amount of terpineol would also lead to insufficient binding between the polymer matrix and MWNTs dispersed in the composite. Based on the FTIR analysis shown in Fig. 4.6b, it could be observed that the decrease in IR transmission peak at 3444 cm^{-1} for composites with increased amount of terpineol, as compared to virgin PPP, should be attributed to the interactions between terpineol and PPP (Vaisman et al., 2007). These results would confirm the fact that the presence of terpineol in MWNT/PPP composites would affect the compatibility between MWNTs and PPP.

In order to examine integrated effect on MWNT/PPP composite preparation, the amount of terpineol and ultrasonicated compounding time were intentionally varied. The composite prepared with 2.0 mL terpineol and compounding time of 20 min was labeled as composite A, while composite B was prepared with 2.5 mL terpineol with compounding time of 10 min, and composite C, with 2.0 mL terpineol and compounding time of 10 min. Fig. 4.7 shows typical electrical response of sensors prepared from the three composites with toluene exposure time of 10 min in each cycle. After regeneration by exposing the sensor to dry air for a certain time period (not shown in the figure), toluene concentration was increased stepwise from 2.3 to 4.7 and 7.0 vol%. It should be noted that the sensor prepared from each composite exhibited different initial resistance, which was 330 kΩ for the composite A, 105 kΩ for composite B and 44 kΩ for composite C. It could be seen that the thin-film sensor prepared from composite C did not exhibit significant change in response even when the gas concentration was increased. On the other hand, the sensor made of composite A provides the most detectable change. The gradual decrease of the overall resistance of a composite film could be attributed to the gradual change of the intrinsic properties of MWNT and PPP contact within the composite film. The absorbed toluene could not be completely removed from the composite when it is exposed to pure nitrogen flow for regeneration.

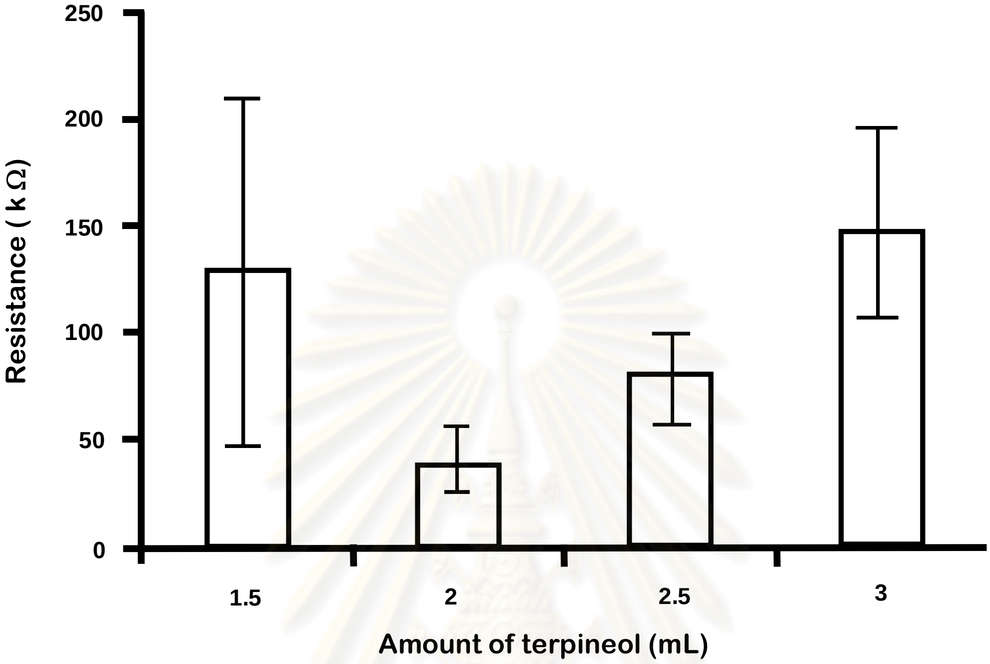


Figure 4.6 a Influence of amount of terpineol on initial resistance of MWNT/PPP composites.

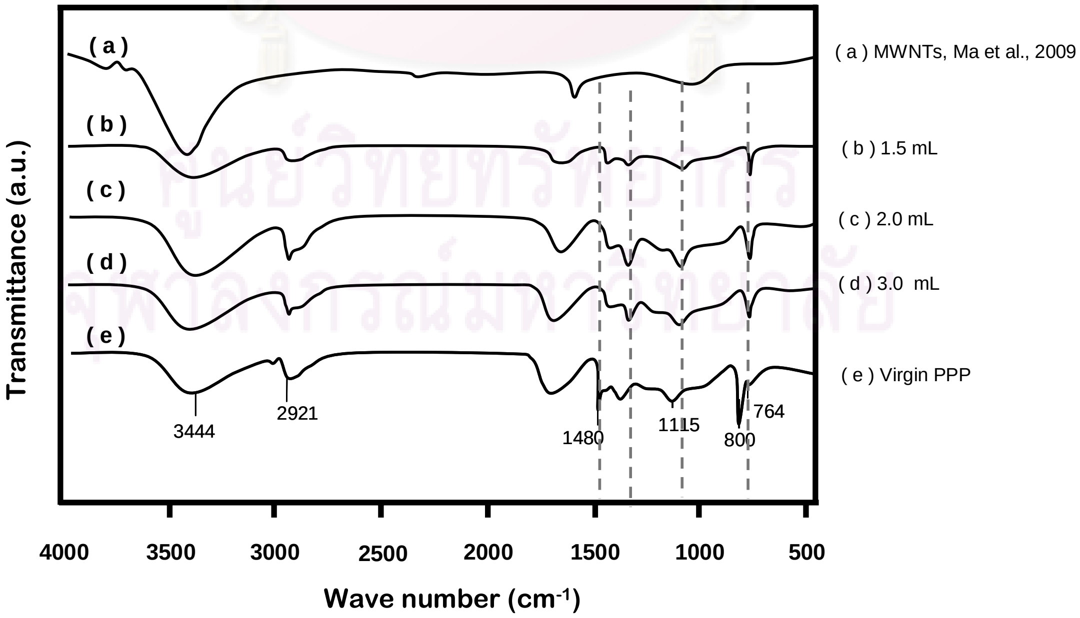


Figure 4.6 b FTIR spectra of MWNT/PPP composites with different amount of terpineol.

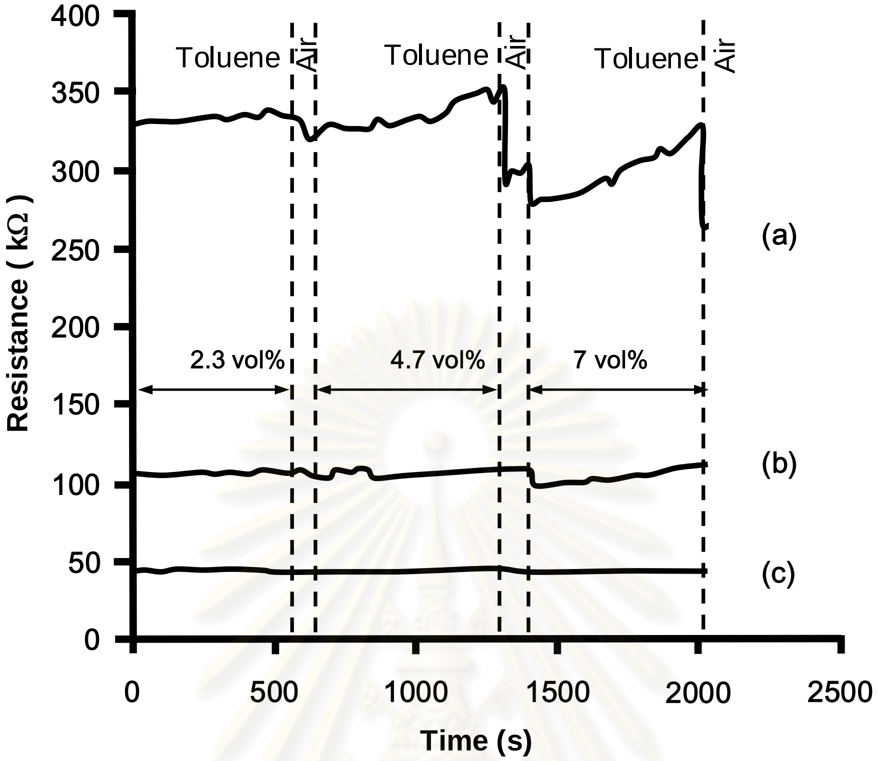


Figure 4. 7 Change of electrical responses of MWNT/PPP composites with different toluene concentration: (a) composite A, (b) composite B and (c) composite C.

Fig. 4.8 shows graphics obtained from Fig. 4.7 when analytes injected 7 vol% (0.0028 gmol/L) Some selected points within range of 1200-2000 s. are used to calculate the sensitivity. Using formula $S = (R - R_0)/R_0$ where R is the resistance at any time and R_0 the initial resistance of the composite (Zhang et al., 2005), the sensitivity of sensors remarkably increased with time elapsed after toluene with higher concentration was introduced into the testing chamber. Maximal sensitivities of 15, 12 and 2% were detected for the thin films of composites A, B and C, respectively. The change of electrical resistance of these composite thin films would be attributed to change of their microscopic structure. When the composite was exposed to toluene, it could adsorb toluene and then the toluene could interact with the polymer matrix, leading to a swelling phenomenon. The swelling phenomenon would affect the microscopic structure inside the composite by suppressing the contact between entangling MWNTs dispersed in the polymer matrix. As a result, the tunneling current between nanoparticles in the matrix would become lower (Zee and Judy, 2001). In addition, gas adsorbed in the polymer would also cause change in the near-surface charge carrier (electron holes) density by its interactions with MWNTs.

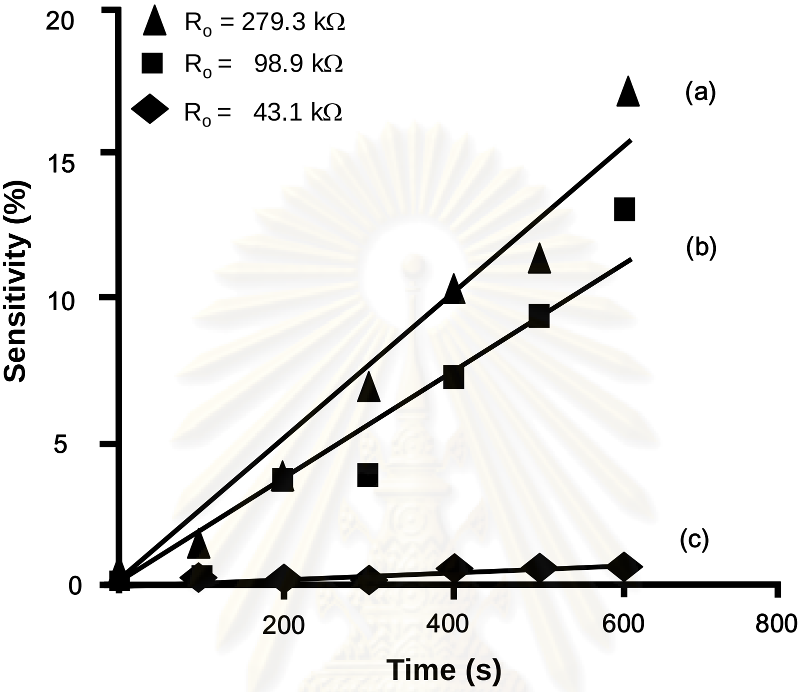


Figure 4. 8 Electrical sensitivity of MWNT/PPP composites exposed to toluene with concentration of 7.0 vol.% (0.0028 gmol/L): (a) composite A, (b) composite B and (c) composite C.

An increase in resistance could also be caused by the reduction of electron flow within the composite (Santhanam et al., 2005). Our experiment showed that swelling in the composite with higher initial resistance was more rigorous, resulting in higher sensitivity in electrical resistance change. Also, based on microscopic analysis, the swelling phenomenon which would significantly change the composite film structure is worth further investigation. In summary, this work revealed that MWNT/PPP composite thin films, prepared by simple polymerization with the assistance of ultrasonication, possessed intrinsic electrical resistance which depends on compounding time and amount of added binder. The optimal condition for preparing MWNT/PPP composite which was sensitive enough for detecting toluene would be 20 min compounding time with the addition of 2.0 mL terpineol. Further improvement for fabricating sensors using MWNT/PPP composite with faster response and higher sensitivity to relatively low concentration of gaseous pollutant would be an important issue and challenge.

The comparison with other result (Parikh et al, 2006) shows that MWNT/PPP composite no sensitive to toluene. The work of Parikh et al. (2006), used 1 vol% of toluene with involving SWNT while in this experiment employed around 7 vol%.

4.4 Response to Other Chemical Vapor

Generally, the properties of film will determine the response of sensor (Ma et al., 2006). Therefore, polymer matrix easily makes contacting with molecules from analytes having similar solubility parameters (Dong et al., 2004). PPP composite gave different sensitivity to vapor exposed as shown in Fig 4.9. All the analytes in Fig. 4.9 and Fig. 4.10 caused increasing the electrical resistance of composite when the electrode was exposed to vapors.

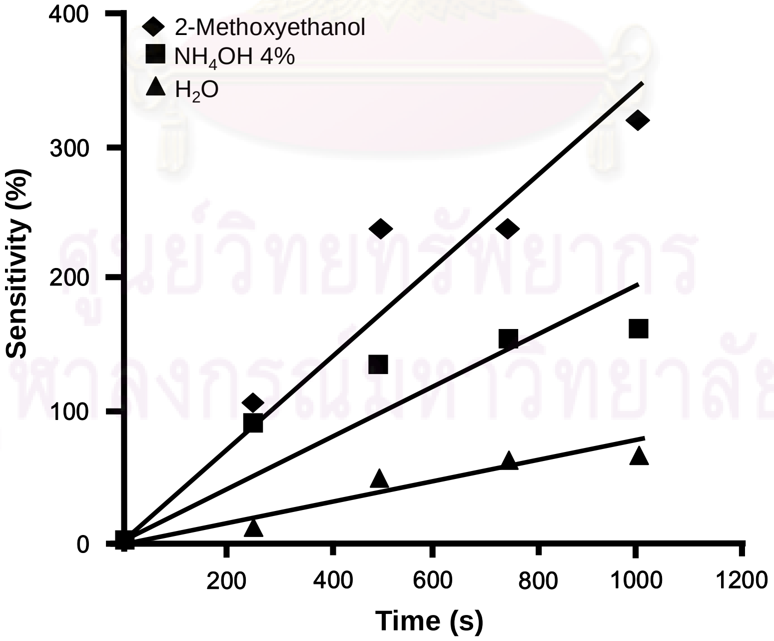
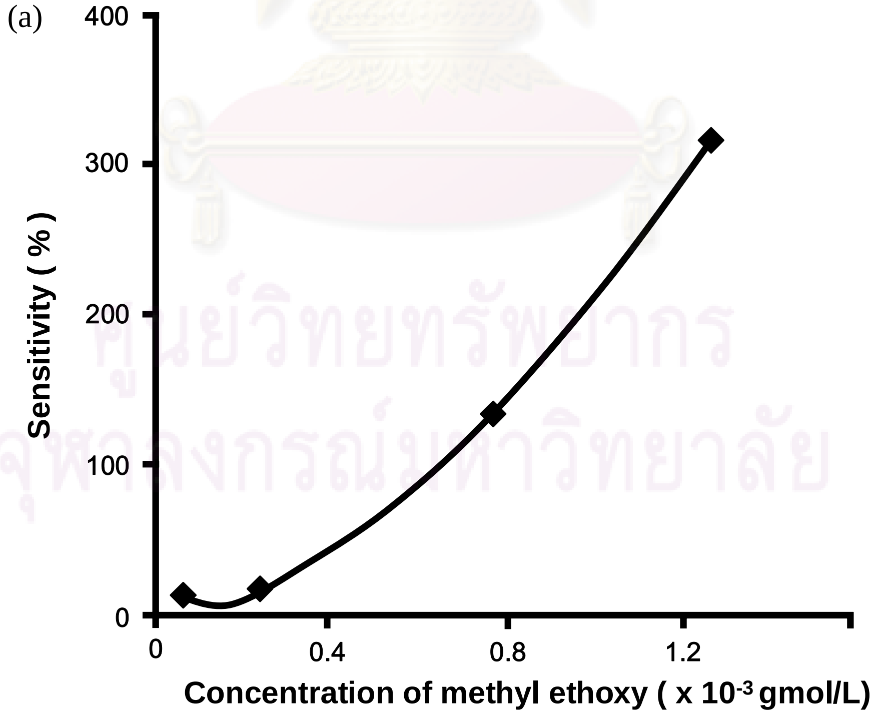


Figure 4. 9 Sensitivity of the composite made of 5 wt.% MWNTs on 2-methoxyethanol, NH_4OH 4%, and water vapor with same volume (0.1 mL).

Fig. 4.9 shows the sensitivity of PPP composite containing 5 wt% of MWNTs when it was exposed to three analytes. Through the results, MWNT/PPP composite is relatively very sensitive on 2-methoxyethanol (ME) compared to other analytes tested. Within 1000 second ME reaches sensitivity of 320%. This effect probably results from favorable π-π van der Waals interactions between ME analyte and the PPP composite giving significantly enhanced response to ME. Both OH and O group in ME take interaction with benzene ring of PPP changing resistance in the composites. Water vapor containing of 4 vol% ammonium hydroxide could be detected by MWNT/PPP composite. The sensitivity of water vapor containing NH_4OH lies between water and ME vapor. This reveals that NH_4OH, implicitly NH_3, determine the response. This shows that the composite is useful for ammonia detection. The detection of ammonia generated by liquid ammonia has been reported by (Li et al., 2008).



(b)

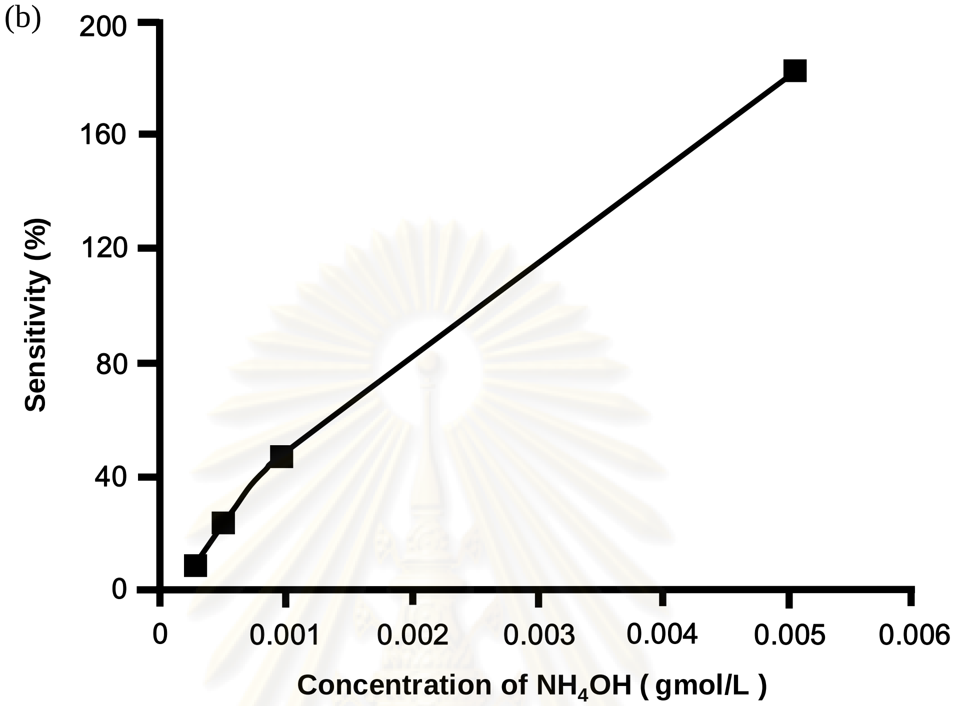


Figure 4. 10 Sensitivity of MWNT/PPP composite on (a) 2-methoxyethanol in various concentration, (b) NH_4OH 4 %.

Fig. 4.10a shows the sensitivity of composite on ME and NH_4OH. The lowest concentration of ME in chamber detected was 0.6 10^{-3} gmol/L. Increasing of ME concentration more than 3.1 gmol/L leads to increase sensitivity dramatically. A large amount of ME molecules hinder conductive path more. The OH and H group immediately distributed homogenously trough composite area when a large amount of ME dropt in chamber. In Fig. 4.10b water and ammonia makes interaction with the composite causing the obstacle electron flow in the composite. As shown, water has contribution to increase electrical resistance of the composite. The water molecules adsorbed on the nanotube’s surface as physisorption (Yu et al., 2006). Ammonia dissolved as NH_4OH is playing role in interaction with matrix therefore the resistance of composite changed. A decreasing of holes on PPP composite and charge transfer between anlayte and composite determines increasing electrical resistance of the composite (Chen et al., 2007). These results seem contrary to reports discusses about decreasing of MWNTs. As reported when MWNTs take interaction with NH_3 its resistance will be decreased (Nguyen et al., 2007). This change is due to the electrons transfer from gas molecules to the nanotubes. Therefore, an increasing of electrical resistance when composite in touch with NH_4OH reveals PPP dominated mechanism of electron transfer analyte-composite.

Detection of various analytes is represented in Table 4.1. The results show the PPP composite could detect selected gases, chemo selectivity. In our experiments, the resistance always increases upon exposure of the MWNT/PPP composite film to vapors regardless of vapor type (Parikh et al., 2006). The properties of film such as physical and chemical properties determine the response (Lucci et al., 2005, Arshak and Gaidan, 2005). Other factor such as activity coefficient (Horrillo et al., 2004), permittivity, molecular weight (Zeng et al., 2007), polarity (Parikh et al., 2006) are among the factors responsible for responsivity of material sensor. Analytes acts as a temporary n-dopant or p-dopant. When the electrical resistance and the intertube tunnelling barrier of nanaotubes increased caused by an analyte touching, the analyte is n-dopant (Zaras et al., 2003, Valentini et al., 2004).

It is interesting to note that the composite give comparable response to analytes with OH group. Alcohols and similar structural gave higher response than other analytes. These results are similar to reported by (Paez et al., 2004). In fact, responses on alcohols analytes lead to an idea that the existence of terpineol traced playing role in giving responsivity due to terpineol has alcohol group. However, responses to NH_4OH and HNO_3 imply the dispersant not only the factor. In NH_4OH there are water and NH_3 molecules while in HNO_3 there are water and NO_2 molecules. In this case, molecular weight of analyte does not affect to sensor sensitivity. We think strong interaction among dispersant molecules, PPP and MWNT create a unique property of composites. At the moment the interactions are not clear therefore should be investigated further.

Table 4. 1 Maximum response of composite consisting 5 wt.% of MWNTs on various analytes.

Analytes	Concentration gmol/L (M) (1×10^{-4})	Sensitivity, S (%)	Sensitivity/ conc. (S/M)
Hexane	7.6	1.51	1,986
Acetone	13.5	9.22	6,812
Tetrahydrofuran	12.3	8.38	6,795
Xylene	8.3	3.27	3,945
Benzene	11.2	3.03	2,707
CCl_4	10.3	6.41	6,191
Ethyl acetate	10.2	9.34	9,122
Dimethyl acetamide	10.8	65.05	60,078
Ethylene Glycol	17.7	20.48	11,574
Formaldehide	27.1	83.39	30,809
Ether	9.6	1.79	1,859
Methanol	24.7	42.97	17,384
Ethanol	17.1	37.21	21,694
Isopropanol	13.1	32.75	25,034
NMP (N-Methylpyrrolidone)	10.4	18.02	17,359
Aq. solution of HNO_3 (4%)	55.5	12.36	2,225

The differences of sensitivity of analytes might come from the polarity of analytes (Chen et al., 2005). Hexane, xylene, benzene, ether are non-polar chemicals therefore the interaction with the composite not so high. In contrary, the alcohols are polar chemicals as well as terpineol. The interaction between alcohol vapor and dispersant molecules banded to the composite is easy enabling the vapor molecules blocking the conductive path.

4.5 Characterization of WO_3

Fig. 4.11 shows that transformation of tungsten oxide from precursor. After ATP were mixed with the hydrochloric acid the precursor changed to like-clay form as shown in Fig. 4.11b. Fig. 4.11c-d show different formation of tungsten oxide. It is clear that the acid has influenced the final formation of tungsten oxide. These facts explain that beside temperature (Guidi et al., 2004) there is another aspect that influencing formation of size of tungsten oxide. An interesting phenomenon is shown by last two figures. The form of tungsten oxide in Fig 4.11d is like-ball while Fig 4.11e like-plate. It might be assumed that interaction glycerol, ferocene, tungsten oxide, and trace of acid in precursor have effects to the final formation. This phenomenon should be investigated further.

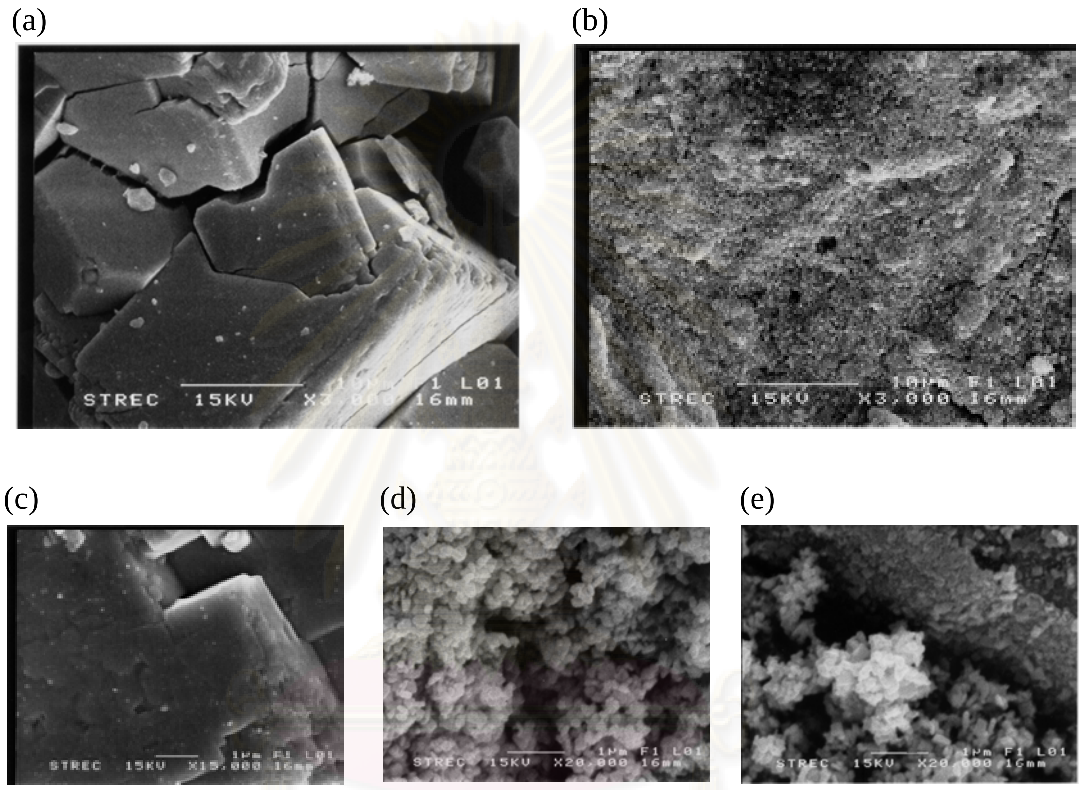


Figure 4. 11 SEM of (a) precursor ATP, (b) pretreatment-ATP with HCl before sintering, (c) tungsten oxide after sintering from not pretreatment-ATP and mixed with synthesized-CNTs, (d) pretreatment-ATP without CNTs, (e) pretreatment-ATP after sintering with CNT.

Guidi et al reported that temperature influences the dominant structures in tungsten oxide. At high temperature more than 750 °C monoclinic (γ-WO_3) structures are dominant. XRD analysis showed the presence of the orthorhombic phase (β-WO_3) for the powders annealed at 450 and 550 °C. At the intermediate temperature of 650°C, coexistence of the two phases was found up. Nishide and Mizukami (1996) showed that tungsten oxide exhibited high intensity when the compound fired above

700^{o}C. The peaks at 2θ = 20-25 explain that crystal is tetragonal. The tetragonal structure characteristically shows two large peaks in the 23-25° region with d values of 0.3900 nm (2θ = 22.80°) and 0.3700 nm (2θ = 24.05°).

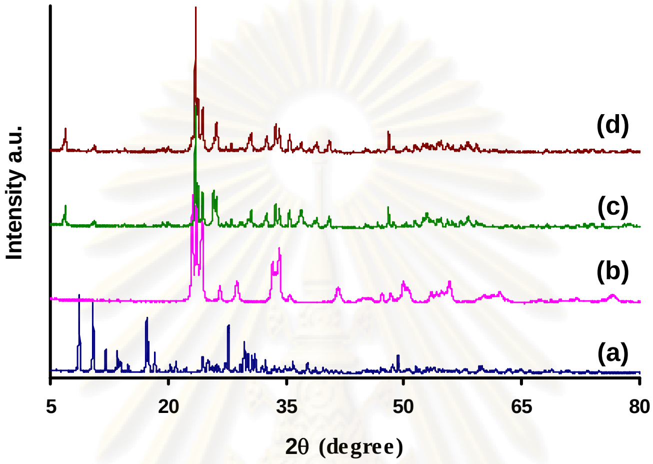


Figure 4. 12 XRD pattern of (a) Virgin ATP, (b) tungsten oxide without pretreatment-HCl with CNTs, (c) tungsten oxide with pretreatment HCl without CNTs, (d) tungsten oxide with pretreatment HCl with CNTs.

Fig. 4.12 shows there were changing of material structure after ATP (Fig. 4.12a) sintered at 740^{o}C. Structure of tungsten oxide in Fig 4.12b consists of two types monoclinic with different in beta angle 115^{o} and 120^{o} respectively. First monoclinic with lattice points a =18.3340, b=3.7860, c=14.0440 with dominant peak at 2θ=23.4822 match with $W_{18}O_{49}$ (JCPDS, 71-2450). Second monoclinic with a=5.5769, b=4.8986, c=5.6644 are match with WO_2 at 2θ=25.7818 (JCPDS, 5-431).

Products of precursor-pretreated with HCl show similar peaks, Fig. 4.12c and d. The analysis reveals that both products are monoclinic. The beta angle for Fig. 4.12c and 4.10d are 90 and 115 respectively. Fig. 4.12c shows dominant peaks are located at 2θ= 24.3169, with a=7.3060, b=7.5400, c=7.6920 which mean match with WO_3 (JCPDS, 83-950). The dominant peak at 2θ = 23.48466 in Fig. 4.12d is match with $W_{18}O_{49}$ (JCPDS, 84-1516).

The BET specific surface areas of the tungsten oxide are reported in Table 4.2. It can be observed that the HCl influences the size of tungsten oxide. It is well known that WO_3 are generally low surface area materials

Table 4. 2 BET characterization of tungsten oxide.

Product type	$a_{s,BET}$ m^2/g
Without pretreatment HCl	3.9364
With pretreatment of HCl without CNT	7.7596
With pretreatment of HCl with CNT	8.1039

4.6 Response of WO_3 Composite on Ethanol

Although tungsten oxide has known very sensitive to gasses such NO_2 (Bi, NH_3, and H_2S (Marquis et al., 2001), the tungsten can be used to detect other chemical vapor. Wang et al. (1995) has fabricated tungsten composite to detect methanol and toluene. Then Papadopoulos et al. (1996) incorporated WO_3 and SnO_2 to detect CO, CH_4, ethanol, butane, and propane. Those results show that the tungsten composite can be applied as sensor material for organic chemical. Hence, for next step we fabricated composite consist of CNTs, PPP, and tungsten oxide with composition 10 wt.%, 54 wt.%, 36 wt.%, respectively.

Fig. 4.13 shows the response of material sensor using different ethanol concentration such as 3.4×10^{-3}, 2.7×10^{-3}, 2.1×10^{-3}, 1.0×10^{-3}, and 0.3×10^{-3} gmol/L, respectively. We call one cycle when the profile of response move from a point at baseline then return to baseline or exceed the baseline. After the first cycle the resistance of composite is lower than baseline. The content of ethanol vapor in composite influences the amplitude of response profile. When the electrode put in the testing chamber at first time the vapor absorbed intensively to the composite. Pulling out of the electrode causes vapor inside chamber going out or air at room going into the chamber. As a result the concentration of vapor in the chamber is decreased. While the electrode in open air, the composite desorbs the absorbed-vapor leading the resistance of composite decreases. The inserting and pulling of the electrode from testing chamber implies on the decreasing of vapor in the chamber and in composite. Therefore, the response of composite to vapor decreases as well as how frequently inserting and pulling.

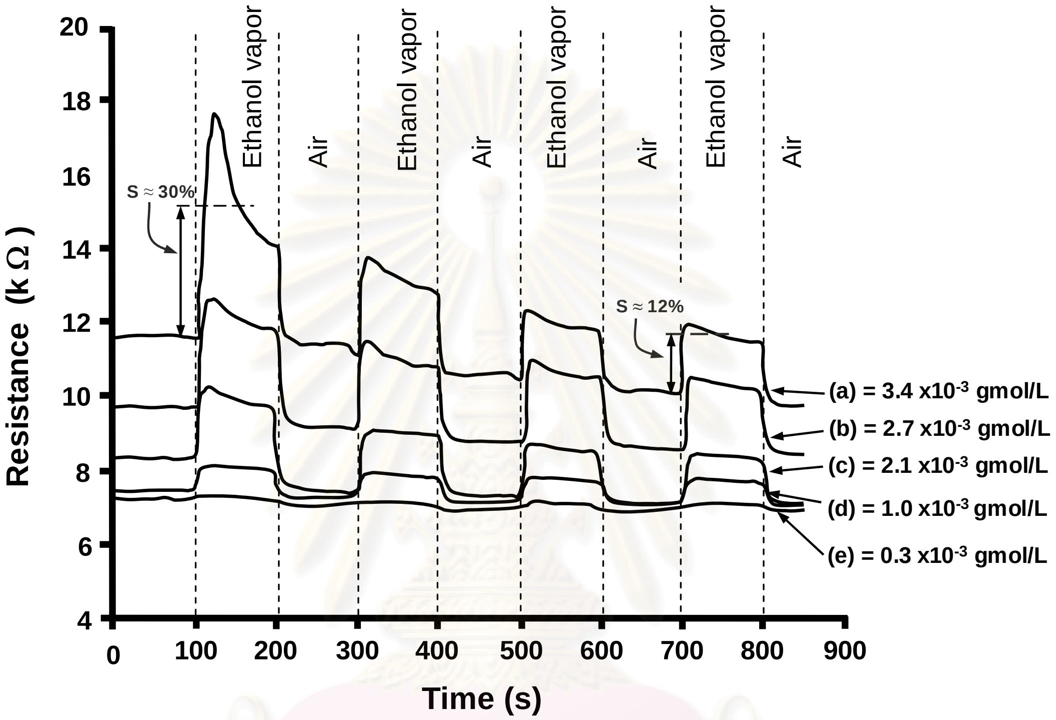


Figure 4. 13 Response of MWNT/PPP/WO_3 composite (10/36/54 in wt.% respectively) on ethanol vapor.

Sensor shows relatively higher responses in high concentration (3.4, 2.7, 2.1 10^{-3} gmol/L) compared the lower concentration (1.0, 0.3×10^{-3} gmol/L). For the lowest concentration sensor can not give response clearly. It seems that in each cycle the ethanol vapor in testing chamber decreases regularly. Pulling out of sensor from chamber or inserting it into chamber enables ethanol vapor composition decreased by air. Ethanol remaining in the chamber every second cycle is estimated of 80 vol% for high concentration and tend to constant for low concentration. At high concentration the absorption molecules of ethanol by composite is intensively hence the resistance increases. The void or sites of composite filled up by ethanol molecule then widen distance of conductive path. During desorption process, the ethanol molecules attract each other and the sites leaved is shrunk. Therefore when composite put in open air the conductive path is adjacent each other leading decreasing in resistance.

To see which component is key factor in response, we have done other experiment. In one experiment we combined two materials to make composite such as MWNT/PPP, MWNT/WO_3, WO_3/PPP, respectively, then in another experiment we used single material. Fabrication of the sensor material was conducted using same procedure as previous experiment.

The response of MWNT/PPP composite on ethanol vapor has been shown in other part, see Table 4.1. The resistance of WO_3/PPP composite was not detectable and during the exposure to ethanol vapor the resistance was unchanged. This fact draws the conclusion that neither WO_3 nor PPP which cause the conductivity in the composite. Other evidences support the conclusion in which the WO_3 and PPP individually could not response of ethanol.

Fig. 4.14 represents the response of MWNT/WO_3 composite on ethanol vapor. At a glance the response of the composite to the vapor similar to response composite displayed in Fig. 4.13. If we compare the response as displayed in Fig. 4.13 and Fig. 4.14 the involving tungsten oxide to combine with MWNTs leads increasing the initial resistance of composite. Then addition of PPP causes decreasing of the initial resistance as shown in Fig 4.14.

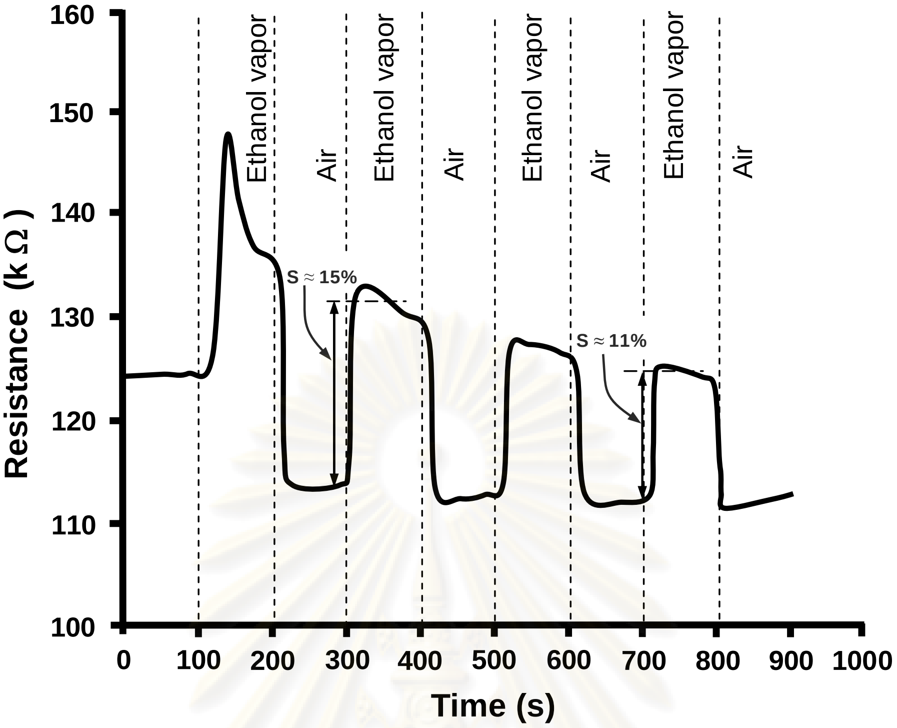


Figure 4. 14 Response of MWNT/WO_3 composite (20/80 in wt.% respectively) on ethanol vapor of 3.4 gmol/L.

. The response of MWNTs on ethanol vapor is shown in Fig. 4.15. At initially the resistance of MWNTs decreases. At that time ethanol vapor donates electrons to reduce the resistance (Sahraei et al., 2009). However, after electrode put in open air the response of MWNTs decreases again. This might be caused by desorbing of ethanol not occurs. Then when electrode put inside testing chamber again, CNTs absorb ethanol vapor until the vapor saturate around MWNTs. Therefore, after the first cycle the amplitude of response displays similarly as shown in Fig. 4.13, and 14. The increasing of resistance when contacted with ethanol vapor has been reported by Paez et al. (2004) and Velentini et al., (2004b). The OH molecules might have taken physisorption interaction with carbon atoms. At the beginning the ethanol transfers electrons to the carbon atoms but after a certain period OH molecules are saturated hence hinders the electron motion leading resistance increase.

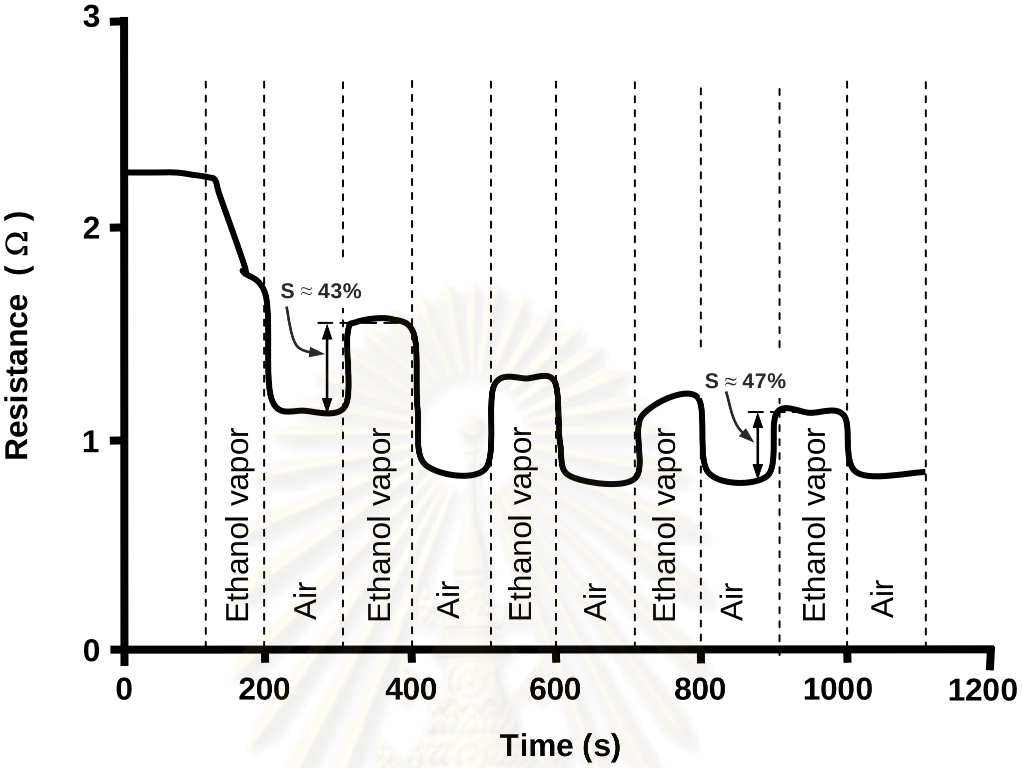


Figure 4. 15 Response of MWNTs on ethanol vapor of 3.4 gmol/L.

Fig 4.16 shows the comparison response of composites. The response of MWNT on exposing of ethanol can not be displayed clearer since the resistance of MWNTs is very low compared to other composites. The results show that the high response of composites is achieved by the composite consisting of MWNTs, WO_3, and PPP. It is showed that the composites involving MWNTs can be effective to give responses of analytes. These phenomena reveal that MWNTs is a key component creating the conductive path. The other materials play role to create a balancing of resistance by which the interaction between analytes and composites could be measured.

However the comparison of response shown in Fig 4.16 raises a question which one of composites is the best performance to detect an analyte. As displayed on Fig. 4.13-4.15 the highest sensitivity to ethanol is MWNTs with sensitivity more than 40% while the other 11-30%. In fact, however, based on Fig. 4.16 the best response is MWNT/PPP/WO_3 composite. It is need additional parameters to determine which one of the composites is the best performance. For instance, as a single component to detect ethanol, the composition of MWNTs is 100%. When MWNTs involved in MWNT/PPP/WO_3 composite the existence of other materials reduces its composition. Therefore, the electrical properties of the composite are not only determined by MWNTs but other materials.

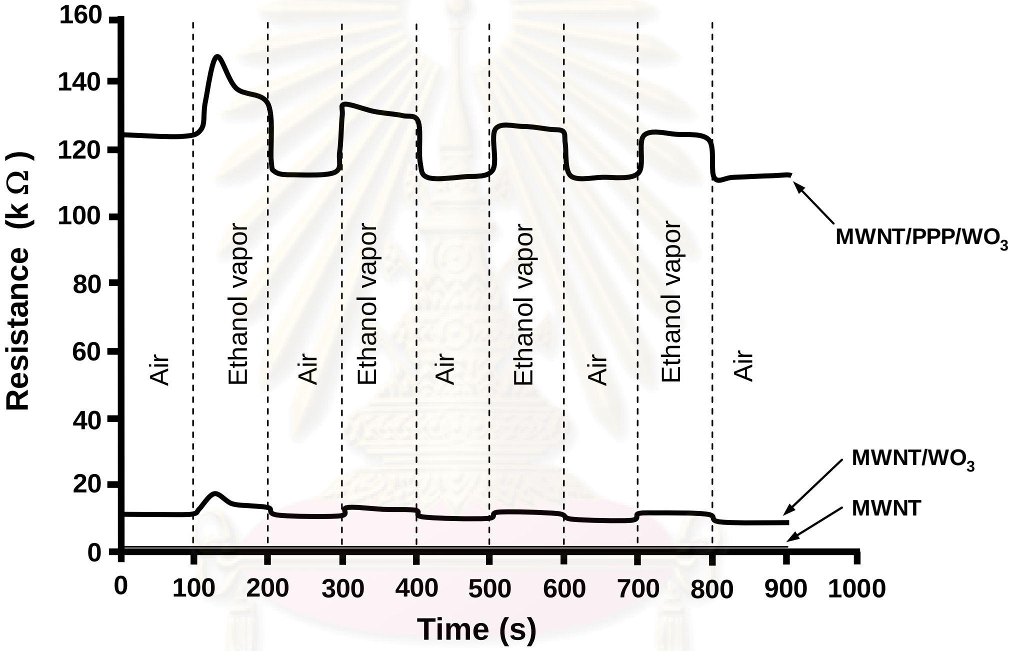


Figure 4. 16 The comparison responses of composites consisting different component.

Fig. 4.17 shows the SEM micrograph of composites used to test response on ethanol vapor. It is clear that the content of composite influence the surface of composites. The MWNTs in composites as shown in Fig. 4.17a and 4.17b is triggering the conductivity in composite. When the MWNTs take interaction with analytes, the molecules of analyte surround the CNTs then donating or receiving electrons. The configuration of CNTs in composites creates conductive path or tunneling among the CNTs. Fig. 4.17c shows composite comprise of PPP and WO_3

which can not be measured its resistance using our multimeter. The involving of tungsten oxide in PPP cannot improve the conductivity of the matrix.

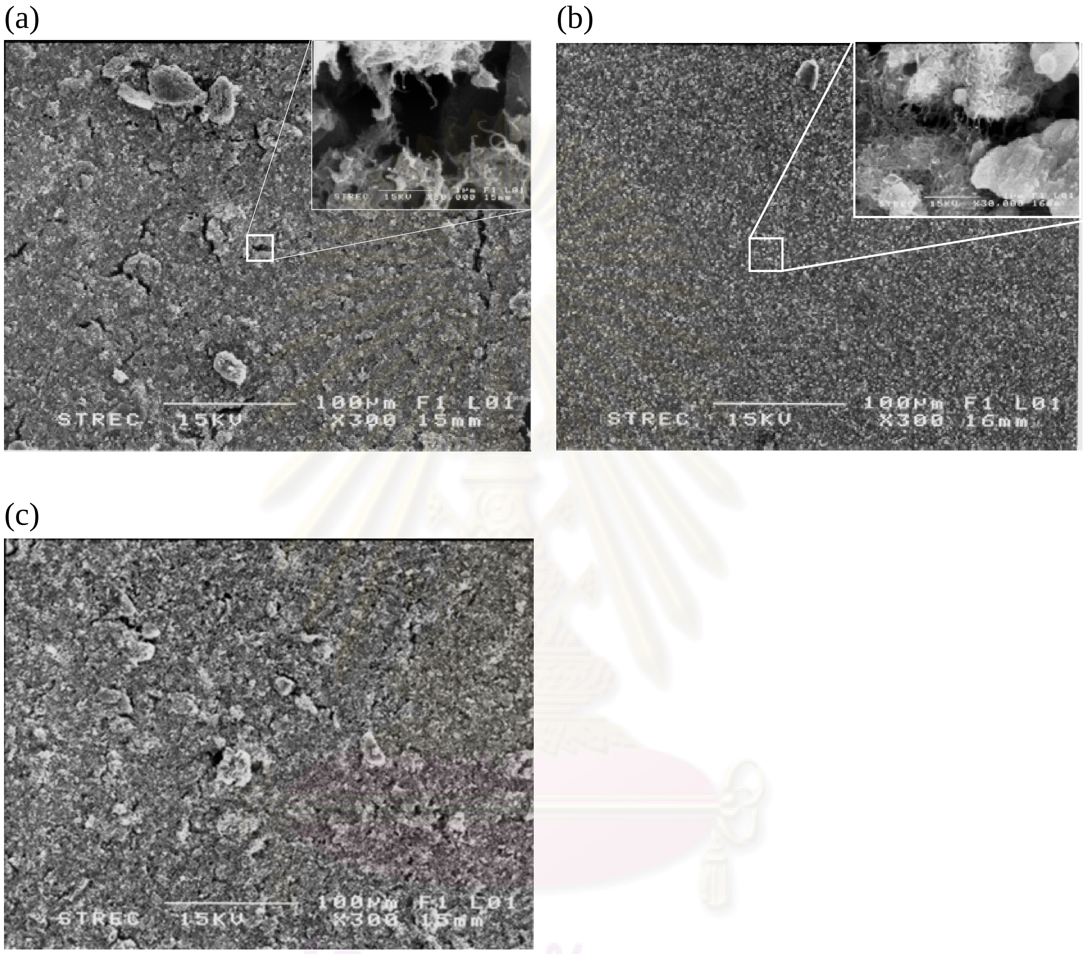


Figure 4. 17 SEM of composites consisting of (a) MWNT/PPP/WO_3 (10/36/54 in wt.% respectively), (b) MWNT/WO_3 (20/80 in wt.%), (c) PPP/WO_3 (60/40 in wt.%).

4.7 Mechanism of Sensing in Sensor Materials Consisting of CNTs

The discussion about alteration of resistance or conductance in sensor materials needs the understanding of mechanism of the resistance or the conductance. For effectively the discussion would be restricted on semiconductor materials only.

Both resistance and conductance basically explains the ability of electrons in a material to move. A material which has a good conductivity indicates the electrons in the material are easily mobile from one point to other points. Reversely electrons in a material with poor conductivity or high resistance are difficult to change their position. In semiconductor materials electrons are able to move when they have energy enough to jump from valence band to conductance band, see discussion 2.6. Normally electrons gained energy to cross a band gap when they are at certain level of temperature. This means that at elevated temperature the resistance of semiconductor materials will be declined.

Semiconductor materials have unique properties concerning of its electrical conductance. The properties called intrinsic and extrinsic semiconductors (Callister, 2003). Intrinsic semiconductor means the band gap energy of material is very narrow therefore electron easily to across it. This character is available for pure materials. In the extrinsic semiconductor the band gap energy is determined by other materials involved or impurities.

In extrinsic semiconductor there are two concepts explaining mobile electrons i.e. n-type and p-type semiconductor. When the impurities make the conductivity of semiconductor increasing the semiconductor called n-type. In this case impurities donate the electrons to semiconductor materials. In contrary when the conductivity of semiconductor materials decreases the material called p-type semiconductor.

The n-type or p-type concept also could be applied to explain the changing of resistance in the sensing mechanism. The interaction between a sensor material and analytes can lead the sensor material be n-type or p-type.

Commercially, there are three types of gas sensors such as solid electrode sensor, catalytic sensor, and semiconducting oxide gas sensor (Moesley, 1995). The sensors work using different mechanisms. The solid electrode sensor works based on the equilibrium of ion. The interaction between gas targeted (or analytes) and sensor causes shift of ion equilibrium. The catalytic sensor is intended to monitor a selective gas by mean combustion reaction between sensor and gas targeted at relatively high temperature. In semiconducting oxide the gas targeted is supposed to make oxidize reaction on the surface at low temperature within certain depth of sensor.

In addition, the alteration of resistance during a sensor material exposed to analytes could also be explained by physical and chemical mechanism. In physical mechanism analytes molecules absorbed into sensor material and make interaction to make electron transfer. The analytes might give its electrons (donor) to sensor material or receive electrons (receptor) from sensor materials. This mechanism is normally occurring for polar analytes or analytes with high conductivity (Valentini et al., 2004, Santhanam et al., 2006, Jeong 2006). After the interaction the resistance of sensor material could be back to its base line.

Using chemical mechanism the analytes react with sensor materials then resistance would be changed (Paez, 2004). In addition the temperature can also influence the response of CNTs-based sensor materials. The electrical properties of CNTs could change with temperature as reported by Li et al., 2006 and Quang et al., 2005.

CHAPTER V

CONCLUSIONS

The synthesizing of a sensor material consists of MWNTs/PPP/WO_3 was successfully done. Unavailable commercially of PPP could be overcome by synthesizing the polymer. The methods to synthesize sensor materials must be based on the comprehensively literature surveys. After that, the characterization of materials synthesized must be put as an important step to reveal phenomena related to sensor materials. An appropriate of characterization methods could help the explanation of something behind the phenomena. Sometimes it is need a standard table to understand the characterization data.

The mixing process is an important step to get composites. It is need to find an appropriate dispersant to get a homogenous mixture. The ratio between a dispersant and particles in matrix is an important condition when MWNTs are involved in a composite.

Regarding to sensing measurement, this step plays role to see accurately the response of sensor materials. There are so many factors which can disturb the measurement. For instance, in air there are oxygen, nitrogen, moisture, very fine of dusts, and other gas in very small quantity. In addition, the material by which electrode made of also influences the responses, in this case electrode made of copper is not so stable. All of the disturbances must be reduced when a response recorded.

A very difficult task in sensor study is to explain confidently what mechanism is important when a sensor material shows its response upon exposing of a gas. Ideally the absorption and desorption of sensor material before and after gas exposing should be observed. Since the sensor materials coated onto an electrode was not much, the method could not be applied. Besides, the property of sensor material could also determine whether the mechanism of response can be explained or not.

Therefore, the interpretation of data could be achieved comprehensively despite the data both in quality and quantity.

Recommendations

The fabrication of a composite as a sensor material needs materials involved distributed homogenously trough the matrix. That means it is need a dispersant as a media to make the homogenous. In polymers case, the dispersant might encompass as solvent by which polymers melt or swollen. Up to know solvents for PPP have not been reported yet. Therefore the functionalization of PPP is required to get a good interaction of PPP with other material especially MWNTs. In addition, the stability of sensor material is another important aspect by which a sensor performance is feasible.

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APPENDICES

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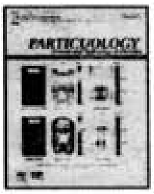

Dispersion of multi-walled carbon nanotubes in poly(p-phenylene) thin films and their electrical characteristics

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ABSTRACT

Dispersion of multi-walled carbon nanotubes in poly(p-phenylene) composite exposed to toluene was experimentally investigated. 3 mg of multi-walled carbon nanotubes with nominal size of 20 nm was compounded with 30 mg of poly(p-phenylene) with the presence of terpineol as binding initiator. To investigate an optimal condition for homogenizing all constituents, ultrasonication with an output power of 750 W was employed with compounding time of 3, 10, 20 and 30 min. With FTIR analyses, it could be confirmed that homogeneous composite of multi-walled carbon nanotubes and poly(p-phenylene) could be prepared. SEM analyses were also conducted to examine the dispersion of multi-walled carbon nanotubes in the polymer matrix. Then intrinsic electrical resistance of the composites after being exposed to toluene was also investigated. It was found that the composite film prepared with ultrasonication for 20 min could provide sufficiently sensitive response with respect to varied concentration of toluene.

1. Introduction

Recently smart material has drawn considerable research interest due to an abrupt increase in various applications to fulfill human needs. Polymer is recognized as versatile materials with many advantages of processing flexibility and controllable physicochemical properties. Therefore, compounding of polymer with nano-scaled particulates for preparing novel composite material has continuously been examined since the invention of conductive polymer (Zarras et al., 2003). To prepare a conductive polymer, conjugation of polymer with other novel materials would be intentionally fabricated. In recent years, polymer compounded with carbon nanotubes (CNTs) has attracted much research attention after its stimulating report of Iijima in 1991 due to its unique physical and electrical properties (Charinpanitkul, Sano, Muthakarn, & Tanthapanichakoon, 2009; Charinpanitkul, Tanthapanichakoon, & Sano, 2009; Iijima, 1991; Li et al., 2007). As a result, research attempts in synthesis and applications of CNTs have been drastically increased year by year.

Meanwhile, there are extensive reports related to utilization of composites of multi-walled carbon nanotube (MWCNT) and polymer for various applications (Kunanuruksapong & Sirivat, 2007; Yuen et al., 2008; Zhang et al., 2005; Zhu, Xie, Xu, & Xu, 2006). One promising application of such composite is fabrication of sensor for monitoring the presence of some specific chemicals. Specifically, modified electrical resistance of polymeric composite consisting of MWCNTs has been found as a useful mean for detecting some specific gases (Zhang et al., 2005; Zhu et al., 2006). Among many polymeric materials, it is well known that preparation of poly(p-phenylene) (PPP) is very simple and economical (Kunanuruksapong & Sirivat, 2007). Therefore, in this study we focus on the dispersion and use of MWCNTs within PPP composite as thin film configuration to detect toluene gas. It should be noted that performance of the fabricated thin film is closely related to its initial resistance. It was found that MWCNTs with relatively large size were difficult to disperse homogenously in molten polymer. To overcome this dispersion problem, melting polymerization, and chemical functionalization incorporated with ultrasonication was carried out. Thereby, investigation of ultrasonication effect on uniformity of MWCNTs dispersed in poly(p-phenylene) was experimentally analyzed by FTIR spectroscopy and electron microscopy. Then the intrinsic electrical resistance of MWCNT/PPP composites prepared under various conditions were examined and discussed.

2. Experiments

2.1. Materials

Poly(p-phenylene) or PPP employed in this work was synthesized in house while MWCNTs with nominal diameter of 20 nm

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Fig. 1. Typical TEM micrograph of pristine MWCNTs employed in this work.

were supplied by Bayer Material Science, Germany. A typical TEM micrograph of the pristine MWCNTs analyzed by transmission electron microscopy (TEM; JEOL2010, JEOL) is depicted in Fig. 1. It could be clearly observed that the MWCNTs entangling with each other have a uniform diameter of 15–20 nm. Procedure for synthesizing poly(p-phenylene) was based on that reported by Kunanuruksapong and Sirivat (2007). Benzene as the monomer for synthesizing PPP was purchased from Panreac Co. Ltd., Spain. Terpineol anhydrous ($C_{10}H_{18}O$) as binding initiator was supplied by Fluka, France. A trace amount of $CuCl_2$ and Al_2O_3 as catalysts was purchased from Riedel-de Haen, Germany.

2.2. Fabrication of MWCNT/PPP composite

PPP and MWCNT with certain weight ratio were compounded by ultrasonic stimulation with the presence of terpineol of designated amount in the range of 1.5–3 mL for the purpose of examining the dependence of the composite characteristics on their preparation conditions. It should be noted that under the initial condition PPP was liquid. Terpineol was employed as the binding initiator for starting the polymerization of PPP with the presence of $CuCl_2$ and Al_2O_3 as catalysts. Compounding time was also varied for investigating its effect on the homogenization of the composite which could be achieved by employing a water bath with temperature control. After a pasty composite was prepared, a few drops of the composite were applied to coat onto a 5 mm × 15 mm alumina substrate consisting of two separate metallic electrodes printed by a sputtering method. A gap of 1 mm is intentionally designed between two metallic electrodes on which the composite film with a dimension of 5 mm × 3 mm would be coated. Therefore, the total area of the composite film to be exposed to toluene gas was 15 mm^2. Five pieces of sensors were prepared for reproducibility test. Before each confirmation test, all sensors were put into an oven for 3 h with a controlled temperature of 75 °C to ensure that excessive amount of organic constituent was removed.

2.3. Characterization methods

Immediately after its synthesis, MWCNT/PPP composite was characterized for its intrinsic chemical bonding by using Fourier transmission infrared spectroscopy (FTIR, Spectrum-I, PerkinElmer). The morphology and dispersion of MWCNT in each composite sample was analyzed using scanning electron microscopy (SEM, JSM 6400, JEOL). To monitor the electrical response of the composite film, each sensor which was prepared from the alumina substrate with copper electrodes connected to the composite was set up inside a 1000 mL glass chamber. Then the sensor was connected to a digital multi-meter (AT-9995 Automotive Meter) and measured signal was recorded by a personal computer. Toluene vapor was introduced into the measuring chamber by dropping calculated amount of toluene using a syringe.

3. Results and discussion

3.1. Effect of sonication

It has been known that addition of MWCNTs into a polymer matrix can significantly reduce electrical resistance of the polymer. The optimal amount of MWCNTs depends on the matrix and size of MWCNTs. Polystyrene, for example, with 10 wt.% of MWCNTs could exhibit a drastic improvement of its electrical resistance (Zhang et al., 2005). For polyamide, reduction of electrical resistance occurs dramatically when the content of MWCNTs is ca. 7–10 wt.% (Zhu et al., 2006). Similarly, PMMA with 4.7 wt.% of MWCNT possesses much lower electrical resistance as compared to the virgin polymer (Yuen et al., 2008). Based on many previous studies (Xie, Mai, & Zhou, 2005; Zhang et al., 2005; Zhu et al., 2006), the addition of MWCNTs will also reduce the resistance of PPP film composite. Therefore, in this study we used 10 wt.% of MWCNTs to prepare

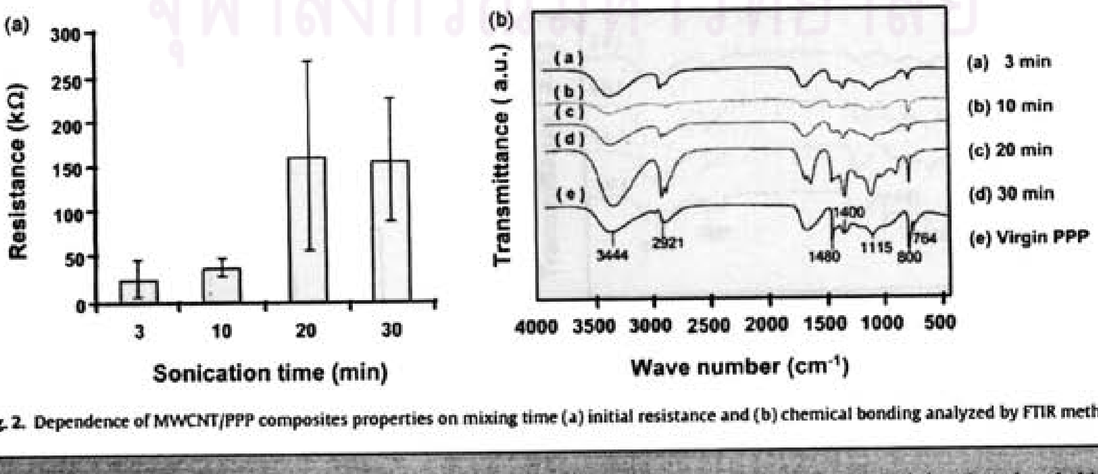

Fig. 2. Dependence of MWCNT/PPP composites properties on mixing time (a) initial resistance and (b) chemical bonding analyzed by FTIR method.

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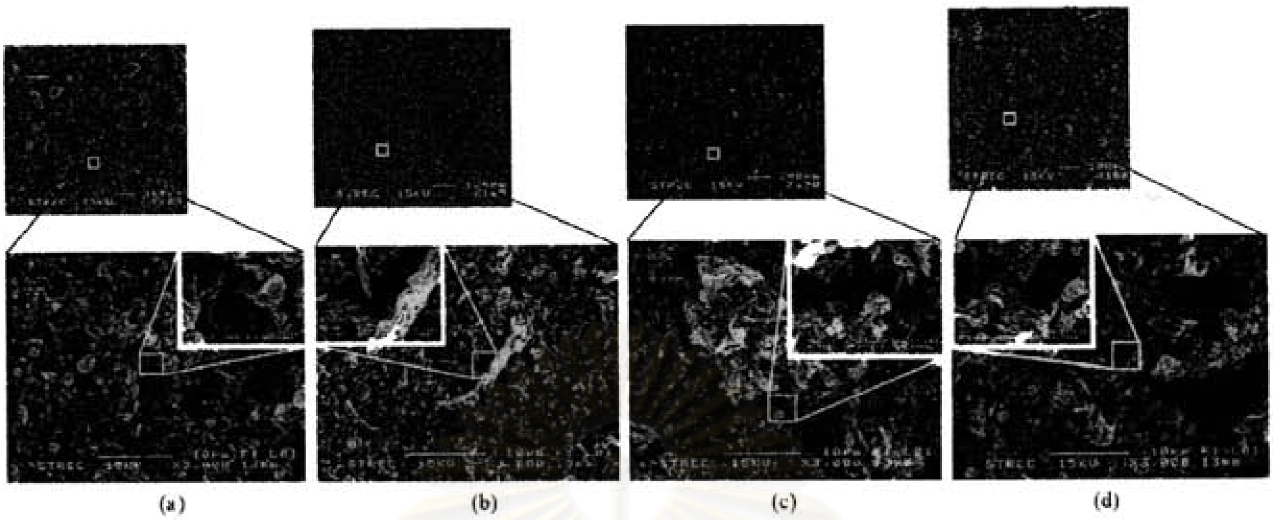

Fig. 3. Comparison of MWCNT/PPP composites prepared with different ultrasonicated mixing time (a) 3 min, (b) 10 min, (c) 20 min and (d) 30 min.

composite films. It should be noted that pure PPP has infinitely high electrical resistance. However, composites of PPP with a certain amount of MWCNTs exhibit electrical resistance in the measurable range of 30–280 kΩ.

Fig. 2a reveals the initial resistance of PPP/MWCNT composites prepared in this work, showing that with compounding time of 10 min the electrical resistance of the composite was significantly low and had the narrowest deviation. Based on the FTIR spectra shown in Fig. 2b, it was also found that composites with compounding time longer than 10 min would exhibit IR transmittance with the same level. It should be noted that the composite prepared with a compounding time of 30 min would exhibit a different spectrum which would be attributed to segregation of MWCNTs from PPP (Vaisman, Watchtel, Wagner, & Marom, 2007; Zhang et al., 2005). These IR spectra reveal that the synthesized polymer has intensive peaks at wave numbers of 764, 800, 1115, 1480 and 2921 cm^{-1}, which confirm the existence of C–H stretching, double side p-substitute stretching, C–C stretching and single side p-substitute stretching of benzene rings, respectively (Kunanuruksapong & Sirivat, 2007). It should be noted that through comparison of IR transmission between virgin PPP and composites, the IR active phonon mode of MWCNT, which could be observed as a peak at 3444 cm^{-1}, gradually increases with compounding time. This evidence indicates that MWCNTs could interact with the PPP matrix (Vaisman et al., 2007).

Furthermore, microscopic analyses using SEM were also conducted for confirming the tendency of MWCNT dispersion in PPP matrix. Fig. 3 presents typical SEM images of the composites prepared by different compounding time with the same amount of terpineol. It could be clearly observed that insufficient ultrasonic compounding time (3 min) could not homogenously disperse MWCNT in PPP, resulting in the composite with non-uniform surface as shown in Fig. 3a. Meanwhile, it should also be noted that heat generated locally by ultrasonication would lead to MWCNT/PPP composite with smoother surface (Fig. 3b and c), although the bulk of composite was already placed in a water bath with temperature control to ensure stable temperature distribution of the composite. Higher magnification clearly reveals that entangling MWCNTs would result in internal connections with conductive paths. However, with the excessive ultrasonication, MWCNT/PPP composite would possibly undergo breakage due to thermal stress (Chen, Jacobs, Wu, Rüdiger, & Schadel, 2007). Also, longer compounding time would result in heat generation to damage the contact between MWCNT and polymer matrix (Fig. 3d), leading to higher resistance of the composite (Xie et al., 2005). As a result, though the composites obtained at the compounding time of 3 min would exhibit the lowest resistance, based on the physical consistency of the composites prepared with the compounding time in the range of 10–30 min, this time range was intentionally selected for further investigations on electrical characteristics.

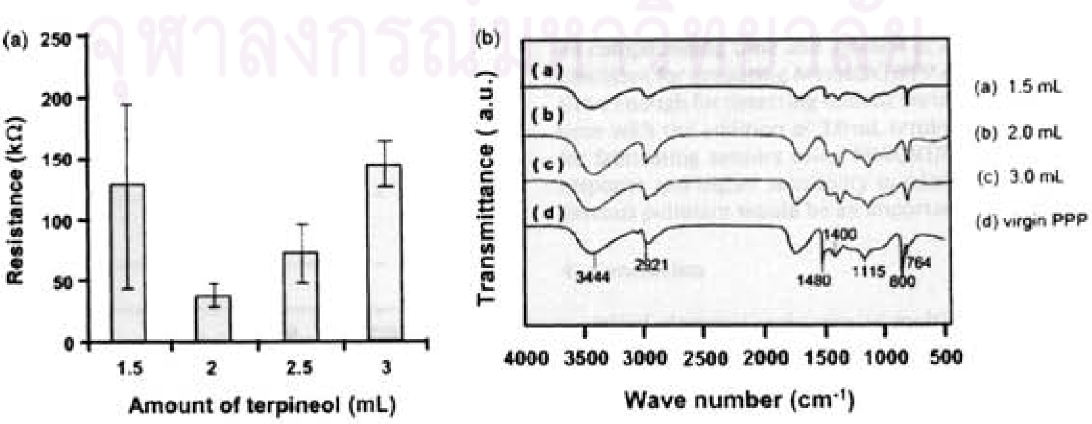

Fig. 4. Dependence of MWCNT/PPP composites properties on amount of terpineol (a) initial resistance and (b) chemical bonding analyzed by FTIR.

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3.2. *Effect of terpineol content*

Fig. 4a reveals that with increasing the amount of terpineol to more than 2 mL given a certain compounding time of 10 min, the electrical resistance of composites increased significantly, though, with 1.5 mL terpineol an increase in the resistance was also observed. This result is attributed to the reason that excessive amount of terpineol would hinder the interaction between MWCNT and PPP. Meanwhile, low amount of terpineol would also lead to insufficient binding between the polymer matrix and MWCNTs dispersed in the composite. Based on the FTIR analysis shown in Fig. 4b, it could be observed that the decrease in IR transmission peak at 3444 cm^{-1} for composites with increased amount of terpineol, as compared to virgin PPP, should be attributed to the interactions between terpineol and PPP (Vaisman et al., 2007). These results would confirm the fact that the presence of terpineol in MWCNT/PPP composites would affect the compatibility between MWCNTs and PPP.

In order to examine integrated effect on MWCNT/PPP composite preparation, the amount of terpineol and ultrasonicated compounding time were intentionally varied. The composite prepared with 2.0 mL terpineol and compounding time of 20 min was labeled as composite A, while composite B was prepared with 2.5 mL terpineol with compounding time of 10 min, and composite C, with 2.0 mL terpineol and compounding time of 10 min. Fig. 5 shows typical electrical response of sensors prepared from the three composites with toluene exposure time of 10 min in each cycle. After regeneration by exposing the sensor to dry air for a certain time period (not shown in the figure), toluene concentration was increased stepwise from 2.3 to 4.7 and 7.0 vol%. It should be noted that the sensor prepared from each composite exhibited different initial resistance, which was 330 kΩ for the composite A, 105 kΩ for composite B and 44 kΩ for composite C. It could be seen that the thin-film sensor prepared from composite C did not exhibit significant change in response even when the gas concentration was increased. On the other hand, the sensor made of composite A provides the most detectable change. The gradual decrease of the overall resistance of a composite film could be attributed to the gradual change of the intrinsic properties of MWCNT and PPP contact within the composite film. The absorbed toluene could not be completely removed from the composite while it is exposed to pure nitrogen flow for regeneration.

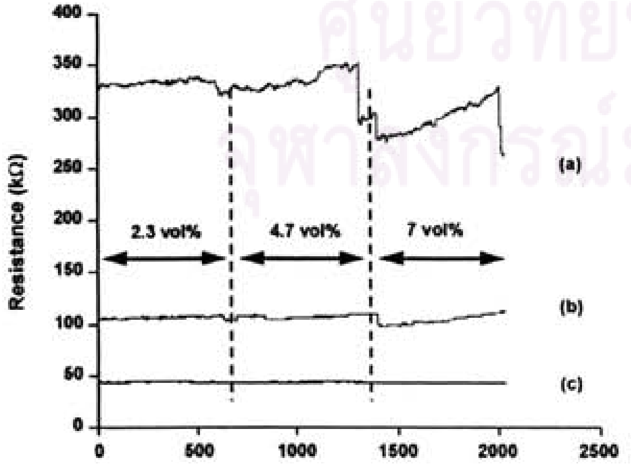

Fig. 5. Change of electrical responses of MWCNT/PPP composites with different toluene concentration: (a) composite A, (b) composite B and (c) composite C.

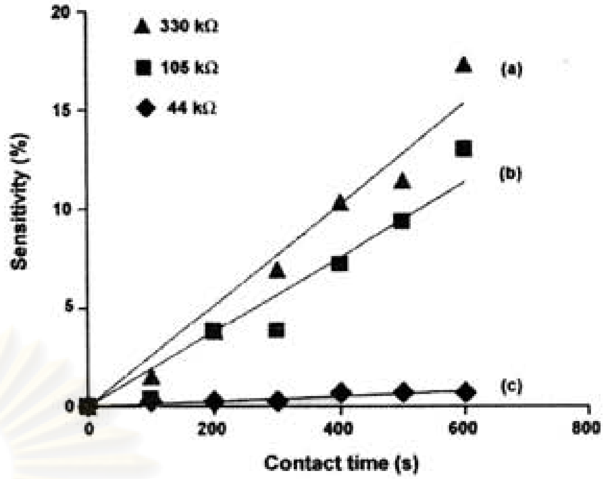

Fig. 6. Electrical sensitivity of MWCNT/PPP composites exposed to toluene with concentration of 7.0 vol%: (a) composite A, (b) composite B and (c) composite C.

Based on results shown in Fig. 6, the sensitivity (defined as $S=(R-R_0)/R_0$, where R is the resistance at any time and R_0 the initial resistance of the composite (Zhang et al., 2005)) of sensors remarkably increased with time elapsed after toluene with higher concentration was introduced into the testing chamber. Maximal sensitivities of 15, 12 and 2% were detected for the thin films of composites A, B and C, respectively. The change of electrical resistance of these composite thin films would be attributed to change of their microscopic structure. When the composite was exposed to toluene, it could adsorb toluene and then the toluene could interact with the polymer matrix, leading to a swelling phenomenon. The swelling phenomenon would affect the microscopic structure inside the composite by suppressing the contact between entangling MWCNTs dispersed in the polymer matrix. As a result, the tunneling current between nanoparticles in the matrix would become lower (Zee & Judy, 2001). In addition, gas adsorbed in the polymer would also cause change in the near-surface charge carrier (electron holes) density by its interactions with MWCNTs. An increase in resistance could also be caused by the reduction of electron flow within the composite (Santhanam, Sangoi, & Fuller, 2005). Our experiment showed that swelling in the composite with higher initial resistance was more rigorous, resulting in higher sensitivity in electrical resistance change. Also, based on microscopic analysis, the swelling phenomenon which would significantly change the composite film structure is worth further investigation. In summary, this work revealed that MWCNT/PPP composite thin films, prepared by simple polymerization with the assistance of ultrasonication, possessed intrinsic electrical resistance which depends on compounding time and amount of added binder. The optimal condition for preparing MWNCNT/PPP composite which was sensitive enough for detecting toluene would be 20 min compounding time with the addition of 2.0 mL terpineol. Further improvement for fabricating sensors using MWCNT/PPP composite with faster response and higher sensitivity to relatively low concentration of gaseous pollutant would be an important issue and challenge.

4. Conclusion

Initial electrical resistance of multi-walled carbon nanotube/poly(p-phenylene) composite could be influenced by the dispersion of MWCNT in PPP, which depends on both compounding time and amount of binding initiator terpineol. Optimal ultrasonicated compounding time could provide a homogenous composite with

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low electrical resistance. In this study, composites with high electrical resistance were prepared with an ultrasonicated compounding time of 20 min, which could provide adequate responses to changing toluene concentration.

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COMPOSITE OF MWCNT/PMMA FOR GASEOUS TOLUENE DETECTION

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Composite of MWCNT and PMMA was prepared by the mean of in-situ polymerization assisted by sonicated mixing. The prepared composites could exhibit electrical conductivity due to conductive path of entangling MWCNT in the polymeric matrix. With the increasing MWCNT content, the conductive path became more uniform, leading to the lower electrical resistivity of the composites. Based on experimental results, the 2.0 wt% of MWCNT to PMMA was considered as the percolation threshold. When the composite was exposed to toluene, the polymer matrix would swell, leading to destruction of conductive path and change of the electrical resistivity of the composites. Dependence of the sensor sensitivity upon the MWCNT was experimentally investigated. With the lowest MWCNT content, degree of swelling in the composite matrix became much higher. Therefore, the electrical resistivity of the composite with the lowest MWCNT content changed substantially.

1. Introduction

Since its discovery in 1991, carbon nanotube (CNT) has drawn attentions from many parts of science and engineering due to its unusual physical and chemical properties (Huang *et al.*, 2005; Iijima, 1991; Nguyen, *et al.*, 2006). Because of its outstanding properties, such as mechanical, thermal and electronic properties, CNT has been expected to use as advanced filler materials in composites. Aslo CNT has been recognized as an ideal candidate for nanoscale sensor devices, owing to its high surface areas due to the existence of the central cores and the outer walls for gas adsorption as well as capability to change electrical properties at room temperature in the presence of different gases (Huang *et al.*, 2005; Lucci *et al.*, 2006; Nguyen, *et al.*, 2006).

In practice, CNT is an excellent material to composite with polymeric matrix with a purpose of gas detection. Therefore, many investigations of composite between CNT and other materials have been conducted by many researches, particularly for improvement of gas detection efficiency (Chen *et al*, 2006; Lucci *et al*, 2006; Zhange *et al.*, 2007). Among various polymers, one of very interesting candidates, PMMA, is selected as the matrix polymer while CNT as a filler. It should be noted that PMMA can be easily processed and fabricated in solid-state forms such as thin films which are often required in most applications. Furthermore, PMMA is sensitive to many kinds of volatile organic compound (VOC). PMMA matrix would swell when VOC molecules are adsorbed into the matrix (Jia *et al.*, 1999)

Meanwhile air contaminations which are related to volatile organic compounds emitted from many industrial settlements have been a chronic problem in various countries. Therefore, a requirement of those toxic gases detection has became an urgent issue for many scientists and researchers to challenge. Among various pollutant gases, toluene was chosen as a target gas because it is widely utilized in many types of products, such as gasoline, spray and paint. Furthermore, it is very easy to contaminate in air and affects to human health. In this work, PMMA is employed as a polymer matrix with dispersion of multi-walled carbon nanotubes (MWCNT) for detecting toluene as a simulated pollutant gas.

2. Experimental

2.1 Materials

Multi-walled carbon nanotubes (MWCNT) were obtained from Bayer MaterialScience Ltd. with a nominal outside diameter (OD) of 5-20 nm, length of about 1-10 μm, number of walls 3-15 and C-purity more than 95%. Methyl methacrylate (MMA) was purchased from THAIMMA Co. Ltd., with 100 ppm of p-methoxy-phenol as inhibitor.

2.2 Experimental procedures

2.2.1Fabrication of CNT/PMMA composites

The mixture between 5 g of MMA and 100 mg of benzoyl peroxide (BPO) was introduced into a 20 ml flask equipped with a reflux condenser and then stirred with a magnetic stirrer for 30 min at 70°C for pre-polymerization. Then a certain quantity of CNT, 100, 125, 150 and 175 mg, was added to the pre-polymerized matrix. Afterwards, the mixture was sonicated for 60min in a water bath with controlled temperature to yield pasty composites (Jia *et al.*, 1999). Uniformity of the blended composite was visually observed before taken to analyze by electro microscopic analysis.

2.2.2 Fabrication of PMMA/MWCNT sensor

A conductive copper electrode was coated onto a plastic strip with a 1 mm gap to make a substrate for testing sensitive properties of PMMA/MWCNT composites. The composites were uniformly coated onto the electrode to form composites films (**Fig. 1**) and put into oven at 70°C for 48 hours to complete the polymerization process.

2.2.3 Toluene detecting experiments

Typical scanning electron microscope (SEM) images of the MWCNT/PMMA composites film were obtained by a field emission SEM instrument (JEOL, JSM-6400). The initial resistivity of each sensor was measured by an automotive digital multi-meter (with TS-232-PC interface). The gas sensing characteristics of the MWCNT/PMMA were investigated by recording its electrical resistivity with respect to exposure time. **Fig. 2** shows a schematic diagram of sensor assessment system in which a fabricated gas sensor was exposed to toluene gas under a controlled condition. Change of electrical reisistivity of the sensor was detected by the same DDM and input to a PC.

The measurement procedure of electrical responsivity was started by heating the left flask to 140°C and toluene with a known quantity was injected into the flask. Afterwards, the vacuumed spherical flask was connected to the left flask by opening the valve between both flasks. Then, pressure in spherical flask would achieve its equilibrium after left for a certain period. Then another valve was opened to draw diluting air into the chamber to adjust the chamber pressure to the ambient pressure. Change of electrical resistivity of the sensor was measured with respect to the exposuring time at a constant temperature of 40°C

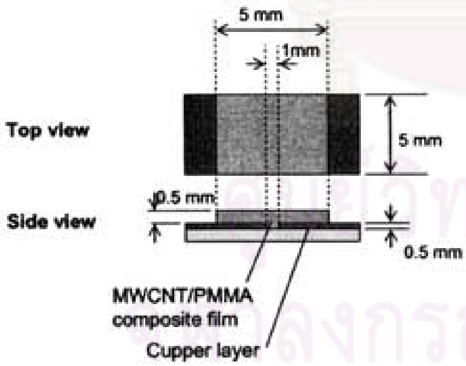


Fig. 1 Schematic diagram of prepared sensor with composite of MWCNT/PMMA

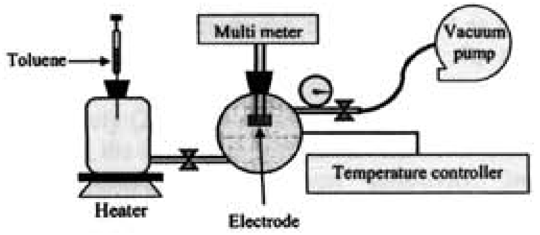
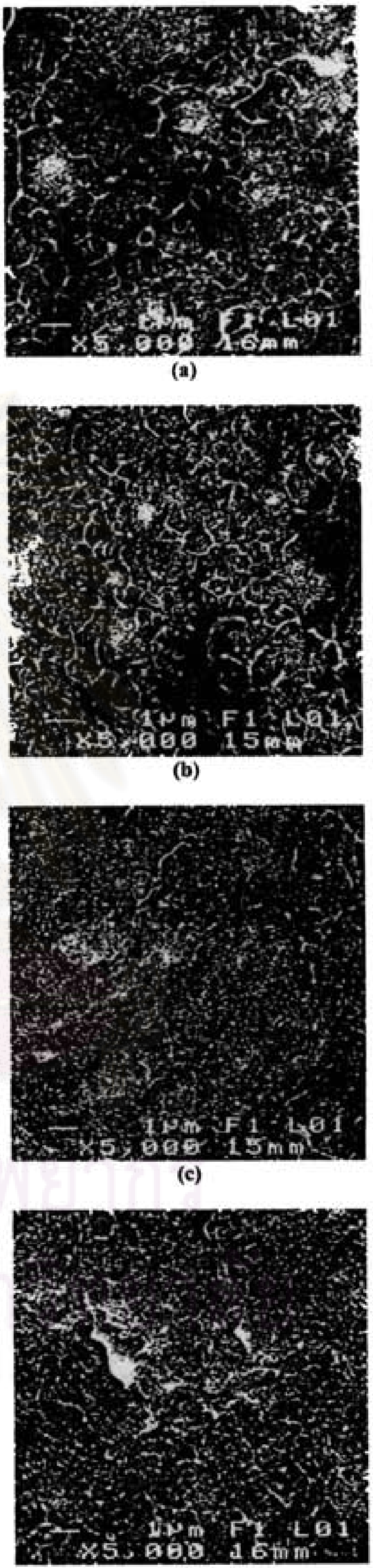


Fig. 2 Apparatus for measuring sensitivity of sensor exposed to toluene



(a)

(b)

(c)

(d)

Fig. 3 SEM images of MWCNT/PMMA composites, (a) 2.0% (b) 2.5% (c) 3.0% and (d) 3.5 wt% of MWCNT

3. Results and discussion

Typical SEM images of MWCNT/PMMA composites illustrated in **Fig. 3** were analyzed for comparison of MWCNT dispersion in the polymeric matrix. The weight ratio of MWCNT to MMA in **Fig. 3 (a), (b), (c) and (d)** is 2.0, 2.5, 3.0 and 3.5 wt%, respectively. It should be noted that ultrasonication could lead to uniform dispersion of MWCNTs in PMMA matrix which is prepared by in-situ polymerization. Liquid monomer with initiator would undergo the polymerization process within the controlled temperature while the MWCNTs were dispersed by the sonication. MWCNT dispersing in the polymeric matrix could be observed as stripes scattering on the dark background. It could be observed that with the increasing MWCNT content; network of MWNCT entangling become more uniform. However, when the MWCNT wt% was higher than 3.0%, the difference in MWCNT dispersion was hardly observed (**Fig. 3 (c) and (d)**).

In general, PMMA is an insulating material but it could exhibit conductivity once conductive additives are introduced. With a sufficient quantity of MWCNT added into the polymeric matrix the conductive path could be formed throughout the matrix, resulting in the conductive polymeric compounds (Jia *et al.*). However, the composite electrical resistivity would decrease due to the percolation effect (Lucci *et al.*, 2006; Zhange *et al.*, 2007). **Fig. 4** shows the relationship between resistivity of the MWCNT/PMMA composites and content of MWCNT added. It is seen that the resistivity of composites substantially decreased by the increasing content of CNT. Electrical responsivity of MWCNT/PMMA composite when it was exposed to toluene was illustrated in **Fig. 5**. The resistivity of the composites became higher when the composites were exposed to toluene for longer period. The change of electrical resistivity of the composite is attributable to swelling of the composites (Niu *et al.*, 2007). When the molecules of toluene were absorbed into the polymer matrix, the interval between polymer segments was increased. Thus the conductive path of the composites polymer was hindered because the mobility of polymeric segment and volume of the system was increased. After swelling, some gap among the entangling MWCNTs would be formed due to the volumetric expansion of the composite. Therefore, electron transfer within the composite would be obstructed (Chen *et al.*, 2006; Niu, *et al.*, 2007; Zhang *et al.*, 2007).

The electrical responsivity of different content of MWCNT in the composites was experimentally investigated. The sensitivity, S was defined as S (%) = $((R_t - R_0)/R_0) \times 100$, whereas R_0 and R_t are the resisitivity of the sensor at its initial and exposure states, respectively (Zhang *et al.*, 2007). As could be observed in **Fig. 6**, the composite with the lowest content of CNT (2.0%) exhibited the highest sensitivity. In our investigation, the 2.0 wt% of MWCNT to PMMA was reasonably considered as the percolation threshold. Below the threshold, the composite electrical resistivity became infinite, resulting in unmeasurable sensitivity. However, with a higher MWCNT content, significant quantity of conductive path still remained even though the composite would swell after exposed to toluene. Comprehensive investigation on the optimal content of MWCNT to MMA, which would provide sensor with the consistent and accurate performance, would be the issue to conduct further.

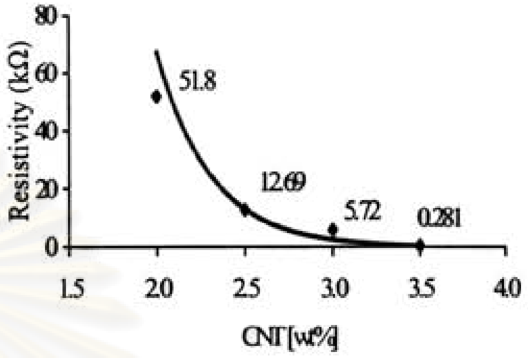


Fig. 4 Resistivity of composites polymer as a function of CNT content

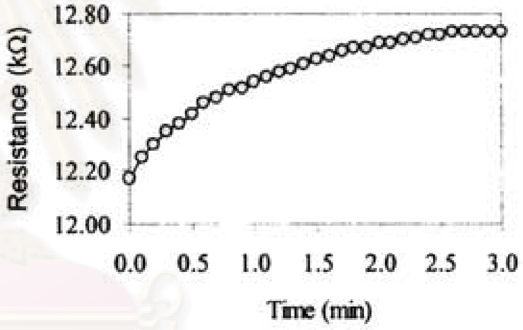


Fig. 5 Resistivtiy change of PMMA/CNT sensors when exposed to 500 ppm toluene (2.5% CNT by weight MMA, 40 °C)

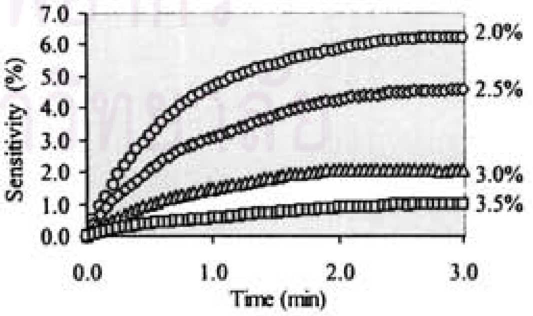


Fig. 6 Comparison of sensitivity of PMMA/CNT with 2.0, 2.5, 3.0 and 3.5 wt% of MWCNT when exposed to 500 ppm toluene at 40 °C

4. Conclusions

With the assistance of ultrasonication, conductive composites could be prepared from the in-situ polymerization of MMA mixed with MWCNT. With the increasing MWCNT content, the conductive path became more uniform, leading to the lower electrical resistivity of the prepared composites. When the composite was exposed to toluene vapor, polymer matrix would swell, resulting in a destruction of conductive path and change of the electrical resistivity of the composites. Dependence of the sensor sensitivity on the MWCNT was experimentally investigated. With the lowest MWCNT content, degree of swelling in the composite matrix became much higher. Therefore, the electrical resistivity of the composite with the lowest MWCNT content changed substantially.

Acknowledgements

This project is collaboration among CU, KU and NANOTEC researchers. A.S. and T.C. would also like to gratefully acknowledge support of the centennial fund of Chulalongkorn University. MWCNT supplied from Bayer Thai Co., Ltd. and MMA from Thai MMA Co., Ltd. are also acknowledged, respectively.

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Niu, L., Y. Luo, and Z. Li; "A highly selective chemical gas sensor based on functionalization of multi-walled carbon nanotubes with poly(ethylene glycol)," Sensors and Actuators B, **126**, 361-367 (2007)

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THURSDAY, JULY 17, 2008

17AM1 Metropolitan

8:00 - 8:30 Asama B, C INFORMATION (Announcement of coming international conferences)

8:30 - 9:20 Asama B, C PLENARY LECTURE
Professor Mauricio Terrones (IPICyT, Mexico)
"Defect Detection and Defect Engineering in Nano carbons: An Alternative Route to Novel Devices"
Chair: Prof. Takuya. Hayashi (Shinshu University, Japan)

9:20 – 9:50 BREAK Metropolitan Lobby 3F, Asama B, Lobby 2F, Sunroute Lobby 3F

17AM2 (ORAL SESSION 10)

Session A
Hotel Metropolitan Room Asama A
NANOTUBES
Chairs: Prof. D. Tomanek (Michigan St. Univ., USA)
Prof. Riichiro Saito (Tohoku Univ., Japan)

17A-am-01 9:50 – 10:20 KEYNOTE LECTURE
Recent Advances in Carbon Nanotube Research
Prof. Mildred S. Dresselhaus[1], Prof. Gene Dresselhaus[1] ([1]MIT, USA) 117

17A-am-02 10:20 – 10:50 FEATURED LECTURE
Manipulating the Current Conductivity of Halide-filled Multi-walled Carbon Nanotubes
Dr. Pedro MFJ Costa[1], Dmitri Golberg[1], Masanori Mitome[1], Yoshio Bando[1] ([1]NIMS, Japan) 117

17A-am-03 10:50 – 11:10
Characterization of the Surface Nature of Carbon Nanotubes by Inverse Gas Chromatography
Hyeon Gu Cho[1], Chong Rae Park[1] ([1]Seoul National Univ., Korea) 118

17A-am-04 11:10 – 11:30
Temperature Effects in Raman Spectra from Single-walled Carbon Nanotubes and Assignments of Their Chiral Indices at High Temperature
Takashi Uchida[1,2], Akira Yamazaki[1,3], Yoshihiro Kobayashi[1,2] ([1]NTT Basic Research Laboratories, Japan) ([2]CREST/JST, Japan) ([3]Meiji Univ., Japan) 118

17A-am-05 11:30 – 11:50
Dispersion and Individualization of Single Walled Carbon Nanotubes through an Alkali Vapor Intercalation Process
Brigitte Vigolo[1], Claire Hérold[1], Jean-François Marêché[1], Patrice Bourson[2], Samuel Margueron[2], Jaafar Ghanbaja[1], Edward McRae[1] ([1]Laboratoire de Chimie du Solide Mineral, France) ([2]Laboratoire Matériaux Optiques, Photoniques et Systèmes, France) 119

12:00 – 18:00 Excursion (Lunch: Oginoya)
Special lectures (Suzaka Mesena Hall)
18:30 - 21:30 Banquet Metropolitan Asama A, B, C

Session B
Hotel Metropolitan Room Azusa
CARBON FIBERS AND COMPOSITES
Chairs: Prof. Michiya Ota (Gunma College of Tech., Japan)
Prof. De Chen (NTNU, Norway)

17B-am-01 9:50 – 10:20 INVITED LECTURE
Carbon-Carbon Composite Material as a Catalytic Reactor
Prof. De Chen[1], Nina Hammer[1], Magnus Rønning[1] ([1]NTNU, Norway) 119

17B-am-02 10:20 – 10:40
Resistance of Multi-walled Carbon Nanotube/Poly (p-phenylene) Composite for Toluene Detection
Adi Ilcham[1], Tawatchai Charinpanitkul[2], Mana Sriyuthsak[1], Apinan Soottitantawata[2], Amornwong Srisurichan[2], Noriaki Sano[3] ([1]Chulalongkorn Univ., Thailand) ([2]Center of Excellence in Particle Technology, Thailand) ([3]Hyogo Univ., Japan) 120

17B-am-03 10:40 – 11:00
Study of Wettability and Reactive Infiltration of Carbon by AlSi Alloys
Javier Narciso[1], Noelia Calderon[1], Rayisa Voytovych,[2] Nicolas Eustathopoulos[2], Francisco Reinoso[1] ([1]Alicante Univ., Spain) ([2]INP de Grenoble, France) 121

17B-am-04 11:00 – 11:20
Acid Modified Cup-Stacked-Type Carbon Nanofibers for Environmental Applications
Guillermo Abdrade-Espinosa[1], Jose Rene Rangel-Mendez[1], Emilio Muñoz-Sandoval[1], Humberto Terrones-Maldonado[1], Mauricio Terrones-Maldonado[1] ([1]Institute for Scientific and Technological Research of San Luis Potosi, Mexco) 121

17B-am-05 11:20 – 11:40
Effect of Carbonization Temperature on Emersion of Nano-structured Carbon Materials in Wood Treated with ACQ
Shuji Yoshizawa[1], Michio Ohata[1] ([1]Meisei Univ., Japan) 122

12:00 – 18:00 Excursion (Lunch: Oginoya)
Special lectures (Suzaka Mesena Hall)
18:30 - 21:30 Banquet Metropolitan Asama A, B, C

Resistance of Multi-walled Carbon Nanotube/Poly(p-phenylene) Composite for Toluene Detection

Adi Ilcham - [1], Tawatchai Charinpanitkul [2], Mana Sriyuthsak [3], Apinan Soottitantawata [2], Amornwong Srisurichan [2], Noriaki Sano [4]

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Abstract

Change of resistance of MWCNT/poly(p-phenyl) composite exposed to toluene was experimentally investigated. 3 mg (10%) of MW-CNTs with nominal size of 20 nm is compounded with 30 mg of poly(p-phenylene) with the presence of 1.5-3 ml of terpineol as binder. To investigate the optimal condition for homogenizing all constituents, ultrasonication with 750 watt output was used for a certain period of 3, 10, 20, 30 minutes, respectively. With FT-IR analysis, it could be confirmed that homogeneous polymeric composite of MW-CNT and poly(p-phenylene) could be prepared. SEM analyses were also conducted to examine the dispersion of MW-CNT in the matrix of the composite. Furthermore, resistance of the composite film coated on conductive substrate was experimentally investigated. It is found that the composite film prepared with 10 minute of ultrasonication could provide the comparatively reliable response with respect to the varied concentration of toluene.

Keywords : MW-CNT, poly(p-phenylene), resistance, composite

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VITA

Mr. Adi Ilcham, the third son of Mr. Ali Ngata and Mrs. Siti Aisyah, was born on 8th June 1971 in Bima, NTB Province, Indonesia. He spent 6 years studying in primary and secondary educations at SMP 1 Bima and SMA 1 Bima, Indonesia. In September 1989, he entered Universitas Pembangunan Nasional "Veteran" Yogyakarta to study in Bachelor of Engineering. In June 1996, he received a Bachelor of Engineering, majoring in Chemical Engineering. In 2003 he graduated from Universitas Gadjah Mada then he continued to study in Doctoral Program at Chulalongkorn University. He was awarded a Doctor of Engineering degree in Chemical Engineering in September 2009.