วัสดุประกอบแต่งของคาร์บอนนาโนทิวบ์แบบผนังหลายชั้นและพอลิเมทิลเมตะไครเลท สำหรับตัวรับรู้สารประกอบอินทรีย์ระเหยง่าย

นาย อมรวงษ์ ศรีสุริฉัน

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MULTI-WALL CARBON NANOTUBE-POLYMETHYL METHACRYLATE COMPOSITE FOR VOLATILE ORGANIC COMPOUND SENSOR

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งานวิจัยนี้นำเสนอการพัฒนาตัวรับรู้สำหรับตรวจจับก๊าซพิษ ซึ่งตัวรับรู้ที่ใช้ได้เตรียมจากสารประกอบแต่งระหว่างท่อคาร์บอนระดับนาโนเมตรแบบผนังหลายชั้น(multi-walled carbon nanotube, MWCNT) และ พอลิเมอร์ชนิดพอลิเมทิลเมตะไครเลท (polymethyl methacrylate) โดยเตรียมสารประกอบแต่งด้วยวิธี อินซิทูพอลิเมอร์ไรเซชั่น (in situ polymerization) และเตรียมตัวรับรู้ด้วยวิธีพิมพ์สกรีน (screen printing method) จุดประสงค์หลักงานวิจัยนี้คือการศึกษาประสิทธิภาพของตัวรับรู้จากสารประกอบแต่งระหว่าง MWCNT/PMMA ในการตรวจจับก๊าซจำพวกสารประกอบอินทรีย์ระเหยง่าย และศึกษาอิทธิผลของตัวแปรต่างๆ ที่ส่งผลกระทบถึงการตอบสนอง (sensitivity) ของตัวรับรู้ ได้แก่ ปริมาณท่อคาร์บอนระดับนาโนเมตรที่เติมลงใน สารประกอบแต่ง ช่วง 2.0 2.5 3.0 และ 3.5 %โดยน้ำหนัก ความเข้มข้นของก๊าซที่ตรวจจับ ช่วง 500 – 1500 ส่วนในล้านส่วน และ ชนิดของสารเคมีที่ก่อให้เกิดไอ ได้แก่ เมทานอล อะซีโตน โทลูอีน และ ไซโคลเฮกเซน

ผลการทดลองพบว่าค่าความต้านทานของตัวรับรู้จะเปลี่ยนแปลงไปเมื่อสัมผัสกับไอของสารระเหย โดยมีเวลาที่ใช้ในการตอบสนองต่ำกว่า 3 นาที นอกจากนี้ยังพบว่าการเพิ่มปริมาณท่อคาร์บอนระดับนาโนเมตรในสารประกอบแต่งจะส่งผลให้ความสามารถในการตอบสนองของตัวรับรู้ลดต่ำลง แต่ในทางกลับกันการเพิ่มความเข้มข้นของก๊าซที่ตรวจจับจะทำให้ตัวรับรู้มีการตอบสนองเพิ่มสูงขึ้น และสุดท้ายพบว่าการตอบสนองของตัวรับรู้จะขึ้นกับชนิดของก๊าซโดยขึ้นอยู่กับปฏิกิริยาระหว่างก๊าซและเมทริกซ์ของพอลิเมอร์

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สาขาวิชา..........วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก..............
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AMORNWONG SRISURICHAN: MULTI-WALL CARBON NANOTUBE-POLYMETHYL METHACRYLATE COMPOSITE FOR VOLATILE ORGANIC COMPOUND SENSOR. THESIS PRINCIPAL ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., 66 pp.

Development of gas sensor for detecting toxic gas was conducted in this research work. The gas sensor was fabricated from composite materials between multi-walled carbon nanotube (MWCNT) and polymethyl methacrylate (PMMA). The composite was synthesized by the in situ polymerization and fabrication of the sensor by screen-printing method. The objective of this research was to investigate the performance of MWCNT/PMMA composite as a gas sensor for detecting volatile organic compound. Furthermore**,** the parameters which affected the response and electrical resistance of the fabricated sensor were investigated**.** MWCNTs content with weight ratio of 2.0, 2.5, 3.0 and 3.5, gas concentration in a range of 500 to 1500 ppm and types of organic gas (methanol toluene acetone and cyclohexane) were experimentally investigated.

The experimental results showed that the increased electrical resistance of the composite was attributed to the exposure to VOC gas, with a response time of less than 3 minutes. In addition, an increased in the MWCNTs content oppositely led to a decrease in the sensitivity of the sensors. On the other hand, the sensitivity was increased with an increased in the gas concentration. Finally, the sensitivity of sensor depended on types of chemical vapor due to interaction between gas molecule and polymer matrix.

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NOMENCLATURES

BPO	Benzoyl peroxide
CNTs	Carbon nanotube
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
MWCNT	Multi-walled carbon nanotube
MMA	Methyl methacrylate
ppm	Part per million
PMMA	Polymethyl methacrylate
SWCNT	Single-walled carbon nanotube
TGA	Thermal gravimetric analysis
VOC	Volatile organic compound

CHAPTER I

INTRODUCTION

1.1 Background

Generally, one of the serious problems in many industrial areas is gas leakage or emission. This may bring a critical impact to the surrounding public and environment. There are many reports and evidences showing that various industrial estates in Thailand have been suffering with this gaseous pollution problem [1]. In order to monitor such gaseous emission, many researchers have consistently tried to develop and investigate various sensor technologies to detect toxic gas efficiently.

Normally, gas sensors can be operated only in some certain temperature range. However, there are increasing demands for monitoring at normal temperature condition. Therefore, new material applicable for low temperature gas sensing has been of interest. At present, one of the most interesting materials is carbon nanotube (CNT). Since its discovery in 1991[2], CNT has drawn attentions from many parts of science and engineering due to its unusual physical and chemical properties. Because of its outstanding mechanical, thermal and electronic properties, CNT is expected to be used as advanced filler in composites. CNT has become an ideal candidate for nanoscale sensor devices, owing to its high surface areas (300-600 m^2/g) available for gas adsorption. Additionally, its capability to change electrical properties at room temperature in the presence of different gases makes it an attractive candidate for gas monitoring [3-6]. Some previous studies showed that the change of conductivity carbon nanotubes was related to gas concentration [6]. Meanwhile, there are some difficulties in employing CNT to fabricate a gas sensor regarding its morphology [3]. Therefore, many investigations of composites between CNT and other materials have been conducted particularly for improvement of gas detection efficiency [6-7]. In this research, one of the versatile polymers, polymethyl methacrylate (PMMA), was selected as the matrix polymer while CNT as a filler. 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 could be swelled when VOC molecules are absorbed into its matrix [8-9]**,** leading to change of polymer volume. For synthesis of polymeric composite it has been reported that in situ polymerization method could provide better results than other methods because uniform dispersion and higher loading could be achieved [6]. Accordingly, the in situ polymerization method was employed in this work.

1.2 Objective of the study

The objective of this research was to investigate the performance of multi-walled carbon nanotube-polymethyl methacrylate (MWCNT/PMMA) composites as a gas sensor for detecting volatile organic compounds.

1.3 Scopes of the study

1.3.1 Prepare MWCNT /PMMA composites by in situ polymerization method with MWCNT at 2.0, 2.5, 3.0 and 3.5 wt%

1.3.2 Analyze morphology and properties of composites.

1.3.3 Fabricate gas sensor by screen printing method with MWCNT/PMMA composite polymer.

1.3.4 Investigate gas detecting performance under various conditions.

1.3.4.1 Gas concentration in a range of 500 to 1500 ppm

1.3.4.2 Types of organic gas, such as methanol, toluene, acetone and cyclohexane

1.4 Procedures of research

1.4.1 Survey and review related literatures.

1.4.2 Design, construct, and install necessary experimental apparatus.

1.4.3 Perform preliminary experiments to find out suitable conditions for preparing MWCNT/PMMA composites.

1.4.4 Fabricate and test the gas sensor under different conditions.

1.4.5 Analyze and conclude the experimental results.

1.4.6 Prepare a manuscript for journal publication and thesis.

CHAPTER II

FUNDAMENTALS AND LITERATURES REVIEW

It is well known that carbon atom has ability to bond with itself and with other atoms in endlessly varied combination of chain and ring forms. At first, only two types of carbon structures, the naturally occurring allotropes diamond and graphite were believed to exist. Until recently another structure Fullerenes, C_{60}, was discovered by two scientists, Kroto and Smalley, in 1985 [2]. Then, syntheses of new carbon structures have been investigated by many scientists. In 1991 the most interesting allotrope, carbon nanotube, was discovered by Iijima [2].

2.1 Carbon nanotubes (CNT)

Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. Many potential applications have been proposed for carbon nanotubes, including conductive and high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and radiation sources, hydrogen storage media, nanometer-sized semiconductor devices, probes, and interconnect. There are two main types of carbon nanotubes, namely single-walled and multi-walled carbon nanotube, available at present [10].

2.1.1 Single-walled carbon nanotubes (SWCNT)

Single-walled nanotube (SWCNT) has a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. SWNT consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap of the tube. Morphology of carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. The end cap structure is similar to or derived from a smaller fullerene. This results in an essentially one-dimensional nanostructure where the length-to-diameter ratio exceeds 10,000 [10-11].

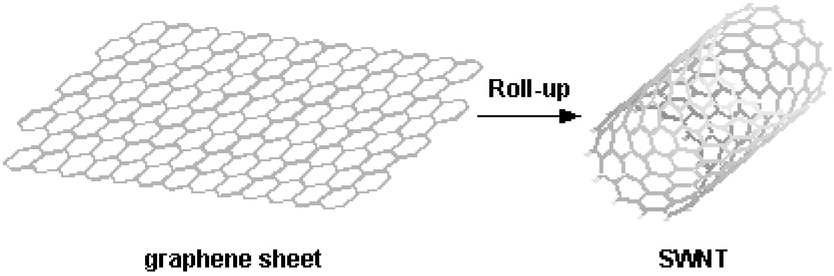

Figure 2.1 Graphene sheet roll up to single walled carbon nanotube [8]

2.1.2 Multi-walled carbon nanotubes (MWCNT)

Multi-walled nanotubes (MWCNT) can be considered as a collection of concentric SWCNT with different diameters. The length and diameter of these structures differ a lot from those of SWCNT and, of course, their properties are also very different [11].

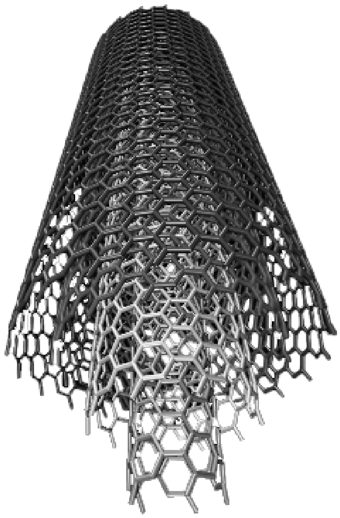

Figure 2.2 Multi-walled carbon nanotube [11]

2.2 Properties of CNTs

The most important properties of CNTs and their molecular background [11] could be summarized below.

2.2.1 Chemical reactivity

The chemical reactivity of CNTs is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNTs surface. Reactivity of carbon nanotube is related to the pi-orbital mismatch caused by an increased curvature [11]. Therefore, a distinction must be made between the sidewall and the end caps of a nanotube. Then, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way.

2.2.2 Electrical conductivity

Depending on their chiral vector, carbon nanotubes with a small diameter are either semi-conducting or metallic [11]. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The differences in conductivity can easily be derived from the graphene sheet properties. The resistance to conduction is determined by quantum mechanical aspects and is proved to be independent of the nanotube length [9].

2.2.3 Optical activity

Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger [11]. Therefore, it is expected that other physical properties are influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.

2.2.4 Mechanical strength

Carbon nanotubes have a very large Young’s modulus in their axial direction. The nanotube as a whole is very flexible because of its great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.

2.3 Gas sensor behavior of CNT [13-14]

In constructing gas sensors, changes in the electrical properties of CNTs, as results of their interaction with analyzes, are used most often. Changing of resistance of the CNTs layer has been used for detection of nitrogen dioxide, ammonia, hydrogen, and some kind of organics vapor generally [14]. From investigations it is indicated that carbon nanotubes behave as p-type semiconductor [13]. When CNTs are exposed to reducing gas, electrons are transferred from gas molecules to CNTs. Then, some positive holes are filled by electrons from gas molecule and this leads to decreasing of electrical conductance of CNTs or increasing of resistance. Then, CNTs are convinced as a candidate for using as a sensor to detecting some kind of gas. On the other hand, oxidative gas molecules will increase positive holes density and the conductance of CNTs.

2.4 **Polymethyl methacrylate (PMMA)** [15]

Polymethyl methacrylate or poly (methyl 2-methylpropenoate) is the synthetic polymer of methyl methacrylate (MMA). This thermoplastic and transparent plastic is sold by the tradenames Plexiglas, Perspex, Plazcryl, Acrylite, Acrylplast, Altuglas, and Lucite and is commonly called acrylic glass or simply acrylic. The material was developed in 1928 in various laboratories and was brought to market in 1933 by Rohm and Haas Company.

Methyl methacrylate monomer has a density of 0.936 to 0.940 g cm^{-3} and a boiling point of 100.5 °C. Methacrylic acid can be converted into high molecular weight product by all the methods used for radical polymerization (bulk, emulsion and suspension polymerization). Polymerization actually leads to cast semi-finished products (sheet, profiles and even tubes). Because of the high degree of polymerization, the cast polymer is distinguished by superior mechanical properties and high surface.

Radical polymerization, which is one of a chain polymerization processes, is a chain reaction involving some sort of active centre. Repeat units are added to the growing polymer one at a time. Usually the reaction does not involve elimination of a small molecule, so it may be called an addition polymerization. Polymethyl methacrylate could be prepared by a process of polymerization as shown in Figure 2.3.

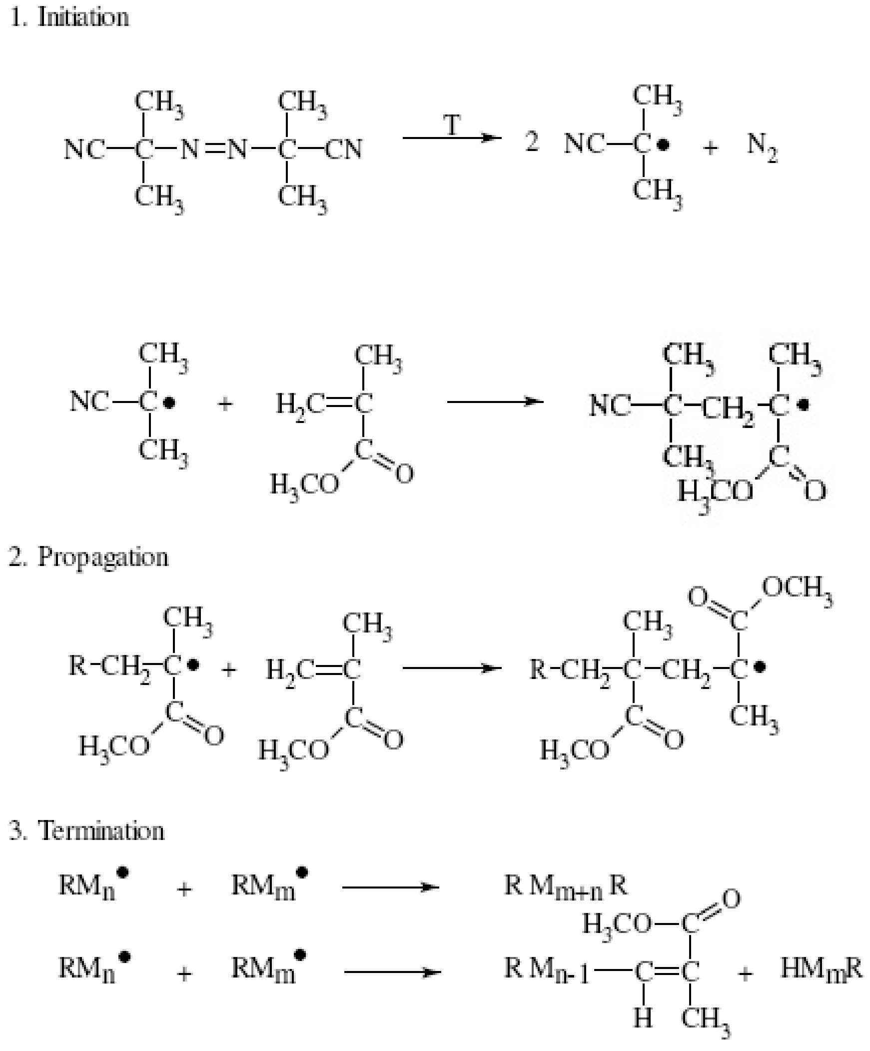

Figure 2.3 Radical polymerization of PMMA [15]

It should be noted that the radical chain polymerization has three stages: initiation, propagation and termination.

Initiation

Initiation involves homolysis of an initiator to give radicals, which then react rapidly with monomer (M) to form monomer radicals.

Propagation

Propagation proceeds by a chain reaction in which monomer adds to a polymer radical, recreating the radical site at the new end.

Termination

The propagating chain keeps growing until the radical site is removed by a termination process. There are various ways in which termination may occur.

The characteristics of polymethyl methacrylates are

- High hardness, stiffness and strength
- Scratch-resistant, high gloss surface capable of being polished
- Water-white transparency; copolymers exhibit inherent yellowish color
- High heat distortion temperature (10 to 50 °C)
- Resistant to weak acids and alkaline solutions as well as to non-polar solvents, grease, oils and water
- High weathering resistance
- Susceptible to stress cracking
- Flammable
- Good processability and machinability

2.5 In situ polymerization [16]

In situ polymerization is a technique for synthesis of composite polymer. The distinguishing characteristic of in situ polymerization is that no reactants are included in the core material. Nanoscale particles are dispersed in the monomer solution, and the resulting mixture is polymerized by standard polymerization methods. One fortunate aspect of this method is the potential to graft the polymer onto the particle surface. Many different types of nanocomposites have been processed by in-situ polymerization. A few examples are silica/Nylon6, titania/PMMA and $CaCO_3$/PMMA. The key to in-situ polymerization is appropriate dispersion of the filler in the monomer. This often requires modification of the particle surface because, although dispersion is easier in a liquid than in a viscous melt, the settling process is also more rapid.

2.6 Swelling of polymer [17-20]

The swelling of polymer matrix arised from the ability of a penetrant to move in a polymeric medium is determined by its transport properties, namely diffusivity and solubility.

In general gas molecule could diffuse into polymer matrix even under a condition below the polymer glass transition temperature. The rigidity of the polymer chains implies that a significant amount of time is needed before even the surface concentration of the penetrant reaches its equilibrium value. In other words, there are time-dependent effects that result from the polymer relaxation time being comparable to the time scale of diffusion. As diffusion proceeds inward, the boundary between the swollen gel and the glassy core moves at constant velocity; this has been determined with optical experiments [17]. They studied the weight gain of sheets of polymethyl methacrylate suspended in a bath of methanol at 24 °C. They observed the movement of the methanol front by coloring the methanol with iodine. Their results revealed a linear weight gain and expansion of polymer plate. Diffusion of gases and vapors in polymers is an important phenomenon of polymer. The diffusive flux of penetrant, one dimension, at steady state can be determined by Fick's 1st law:

$$J = -D\frac{dc}{dz} \tag{2.1}$$

Where J is the flux of penetrant in z direction in units of moles per unit time per unit area, D (assumed constant) is the mutual or interdiffusion coefficient and c is the molar concentration of penetrant

Solubilities of polymer are expressed in terms of the polymer-solvent interaction parameter, χ. This unitless quantity was originally introduced by P. J. Flory [1] and M. L. Huggins [2] as an exchange interaction parameter in their lattice model of polymer solutions. It can be used to predict a miscibility of polymer and solvent. There is thus a critical polymer-solvent interaction parameter is χ_c 0.5. If χ is less than 0.5, it means polymer is soluble in a solvent. The polymer-solvent interaction parameter can be estimated from the corresponding states theory of Prigogine [18]. Correlations using Hansen solubility parameters (HSP) confirm the treatment of the cohesive energy difference term proposed in the Prigogine corresponding states theory. The equation for estimate polymer-solvent interaction parameter is

$$\chi_{12} = \frac{V}{RT}\left[(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2\right] + \beta \qquad (2.2)$$

Where V is the molar volume of the solvent, δ is the solubility parameter for the solvent (1) and polymer (2) while δ_D, δ_P and δ_H are Hansen solubility parameters for dispersion, polar and hydrogen bonding interaction, respectively. R is the gas constant and T is the absolute temperature. The empirical constant β is usually taken to be constant at 0.34. The solubility parameter, δ, is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization. The solubility parameter being equal to the square root of the cohesive energy density is proposed to be used as a numerical value indicating the solvency behavior of a specific solvent.

$$\delta = \sqrt{C} = \left[\frac{\Delta H - RT}{V_m}\right]^{1/2} \qquad (2.3)$$

The cohesive energy density (C) can be derived from the heat of vaporization, in calories per cubic centimeter of liquid, by the above equation, ΔH is a heat of vaporization, R is the gas constant, T is the absolute temperature and V_m is a molar volume.

2.7 Nanostructured composite [21]

For decades researchers have been interesting in composites between polymer and several fillers. They pay attention mostly in macrocomposites, where the length scale of the polymer fillers is in micrometers, as shown in Figure 2.4. The reinforcement length scale is in micrometers. Conversely, nanocomposites, where the length scale of the reinforcement (nanoparticles) is in nanometer scale, become more interesting.

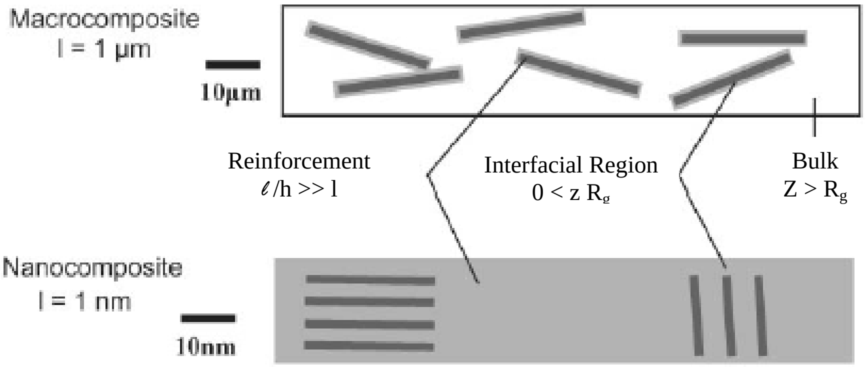

Figure 2.4 Uniqueness of nanostructured materials [21]

The nanocomposites have ultra large interfacial area per volume, and the distances between the polymer and filler components are extremely short. Polymer coils are 40 nm in diameter, and the nanoparticles are on the same order of magnitude as the polymer; as a result, molecular interaction between the polymer and the nanoparticles will give polymer nanocomposites unusual material properties that conventional polymers do not possess. The nanostructured materials, a new branch of materials research, are attracting a great deal of attention because they are available to be used in many applications in areas such as electronics, optics, catalysis, ceramics, magnetic data storage, and polymer nanocomposites. The unique properties and improved performance of nanomaterials are determined by their sizes, surface structures, and interparticle interactions.

2.8 Gas sensor [22]

A gas sensor is a transducer that can detect gas molecule. It normally provides electrical signal with a magnitude proportional to the concentration of gas. Compared with other types of measurement, gas detecting is relatively straightforward. Because there are literally hundreds of different gases, and there is a wide array of diverse applications in which these gases are present. Each application must implement a unique set of requirements. For example, some applications may require the detection of one specific gas, while eliminating readings from other background gases. Conversely, other applications may require a quantitative value of the concentration of every gas present in the area.

2.8.1 Types of gas sensors

There are many different technologies currently available for the detection of gases, each with certain advantages and disadvantages. Five types of most suitable and widely used gas monitors regarding to air quality and safety applications are

2.8.1.1 Electrochemical

2.8.1.2 Infrared

2.8.1.3 Catalytic bead

2.8.1.4 Photoionization

2.8.1.5 Solid state

All of these sensors are commonly used for detection of toxic and combustible gases with some specific purposes to human and property protection or for process control.

2.9 Volatile Organic Compound (VOC)

Volatile organic compounds (VOC) are emitted as gases from certain solids or liquids. VOC include a variety of chemicals, some of which may have short- and long-term adverse health effects [1]. Concentrations of many VOC are consistently higher indoors (up to ten times higher) than outdoors. VOC are emitted by a wide array of products numbering in the thousands. Examples include paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions.

2.10 Literature review

In order to grasp the present situation of new development of gas sensors, some available literatures have been reviewed as follows,

2.10.1 Investigation of carbon nanoparticles based gas sensor

Nguyen Hong Quang et al. [5]

This research investigated about the fabrication of sensors from single-walled carbon nanotubes (SWCNTs) by a screen-printing method. These sensors had been exposed to ammonia (NH_3) gas at room temperature with nitrogen as the carrier gas. The author found that the electrical properties of SWCNTs were different at different temperature or ammonia gas concentration. The SWCNTs were very sensitive to NH_3 gas. It could detect NH_3 in concentration as low as 5 ppm. The sensitivity was increased with increasing gas concentration. A saturation state was established at a concentration of 40 ppm, and the sensitivity of the sensor continued to increase relatively with increasing of concentration levels. The heating and increasing flux rates of carrier gas were used to improve gas desorption. Especially in high temperature it has an effect to behavior of the sensor. At a temperature below 100 ◦C, the SWCNTs exhibited a semiconducting behavior. When the temperature was increased the response was changed to metallic behavior.

Junya Suehiro et al. [13]

This paper described an electrokinetic fabrication method for a gas sensor composed of single-walled carbon nanohorns (SWCNHs) using dielectrophoresis (DEP). To investigate the gas behavior of SWCNHs, SWCNHs were exposed to nitrogen dioxide (NO_2) or ammonia (NH_3) gases while the electrode impedance was monitored. It was found that conductance of SWCNHs sensor increased or decreased upon exposure to ppm-levels of NO_2 or NH_3, respectively. These results were similar to those previously obtained for CNTs gas sensors [5] and suggested that the SWCNH aggregate behaves as a p-type semiconductor same as CNTs. The research revealed that resistance CNTs and SWCNHs were increased when exposed to reducing gas but decreased when exposed to oxidative gas.

2.10.2 Investigation of MWCNT/PMMA composite

V. Skakalova et al. [23]

The objective of this paper was to study the electrical conductivity and mechanical characteristics of nanocomposite from pristine and doped single wall carbon nanotubes with poly(methyl methacrylate). The composite made by mixing PMMA with CNTs. The research revealed that lowest percolation threshold was 0.17 weight percent. Furthermore, the composite had a conductivity value about 17 S/cm. For mechanical properties, a small content of doped carbon nanotube dramatically changed Yong’s modulus, toughness and tensile strength as well.

Zhijie Jia et al. [24]

In this paper, the author had researched about composite between carbon nanotube (CNTs) and poly(methyl methacrylate)(PMMA). The composite was prepared by an in situ polymerization. The experimental results showed that CNTs can be initiated by AIBN to open their p-bonds, which implied that CNTs may participate in PMMA polymerization and form a strong combining interface between the CNTs and the PMMA matrix. Furthermore, both the mechanical properties and the heat deflection temperatures of composites had been found to rise with increasing of CNTs. The dispersion ratio of CNTs in the PMMA matrix was proportional to the reaction time of polymerizing MMA before CNTs were added into the PMMA mixture.

2.10.3 Investigation of carbon nanoparticle/polymer based gas sensor

Bin Zhang et al. [6]

In this paper, authors had investigated about a new kind of conductive polymer composites which was fabricated by the in situ polymerization of styrene (PS) with multi-walled carbon nanotubes (MWCNTs) and by solution mixing of polystyrene with MWCNTs, respectively. Afterward, they studied the electrical percolation behaviors and the resistance responsivities when the composite were exposed to various organic vapors. The experimental results showed that the in situ polymerization method had good efficiency to disperse MWCNTs in PS matrix and produced composites with high sensitivity and rate of response for the vapors of good solvents of PS at filler range from 5 to 15 wt%. They also found that rise in temperature raised the rate of response but lowered the maximum responsivity of the composites. They concluded that the MWCNT/PS composites developed in their work were promising to be used for gas sensors to detect, distinguish and quantity organic vapors.

Yang Li et al. [3]

In this research, a polymeric composite were prepared by direct blending method. Polymethyl methacrylate (PMMA) and multi-walled carbon nanotubes (MWCNTs) were employed as raw materials. Morphology of MWCNT in the composite was analyzed by scanning electron microscopy (SEM). The result showed that MWCNTs were well dispersed in the PMMA matrix. The electrical responses of the composite to methanol vapor were investigated by measuring the changes of electrical response between the ambient environment and a test gas at room temperature. The experimental results showed that a resistance was decreased when the composites were exposed to the reducing methanol vapor, denoting as an n-type response which was fast, reversible and reproducible at room temperature. In addition, the response was not affected by humidity humidity. It was proposed that the n-type, instead of the usually observed p-type, response of the MWCNTs based composite, which was supported by its decreased resistance in the reducing NH_3 vapor, was related to the modification of MWCNTs by the chemical treatment.

Jun Rong Li et al. [7]

In this work, the author prepared a composite polymer-based gas sensor from carbon black and styrene by the in situ polymerization method. The experimental results showed that the composites had selective sensitivity as characterized by high electrical responsivity to the vapors of non-polar and low polar solvents, and low responsivity to the vapors of high polar solvent. Furthermore, conductivity of the composites and absorption characteristics of both the matrix and the fillers exerted important influence on the gas sensitivity of the composites. Therefore, the performance of composites can be tailored by changing filler concentration, molecular weight and molecular weight distribution of matrix polymer, etc. In regard to the fact that most conducting polymer composites as vapor sensing materials are based on crystalline polymer matrices, the approach reported by this paper provided another feasible way to develop new candidates.

Li Niu et al. [25]

In this research a highly selective gas sensor was fabricated by a chemical modification of multi-walled carbon nanotubes containing carboxyl groups (MWCNT-COOH) with poly(ethylene glycol) (PEG) in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC). The resistance responsiveness of the film samples against various organic vapors were investigated. The experimental results showed that the obtained sensors displayed high chemical selectivity, different response and reproducibility depending on the type of organic vapors, which were attributed to the properties of MWCNTs grafted PEG polymers. In addition, the resistance responsiveness was explained by “swelling” and “dissolvation” of polymer matrix by organic vapor.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Multi-walled carbon nanotube (MWCNT) 95% (Bayer Science Ltd)

3.1.2 Methyl methacrylate monomer (MMA) 99.5% (Thai MMA Co. Ltd)

3.1.3 Benzoyl peroxide (BPO) 98% (Panreac Synthesis)

3.1.4 Toluene (C_7H_8) 99.5% (Mallinckrodt Chemical)

3.1.5 Acetone (CH_3COCH_3) 99.95% (VWR)

3.1.6 Methanol (CH_3OH) 99.99% (Fisher Scientific)

3.1.7 Cyclohexane (C_6H_{12}) 99.99% (Fisher Scientific)

3.2 Experimental set-up

The preliminary part of this work was to construct an experimental apparatus for evaluating a MWCNT/PMMA composites behavior. To investigate activity of composite based sensor, measuring equipment was set up as shown in Figure 3.1. The measuring equipment included two chambers, a vaporizing chamber and a testing chamber. The vaporizing chamber with volume of 600 cm^3 was used for vaporizing the VOC. The testing chamber with volume of 550 cm^3 was used for exposing the sensor to VOC vapor. In addition, temperature controller and vacuum pump were set to control temperature and vapor concentration inside the testing chamber. Lastly automotive DMM was used to measure the resistance change of sensor during the experiment.

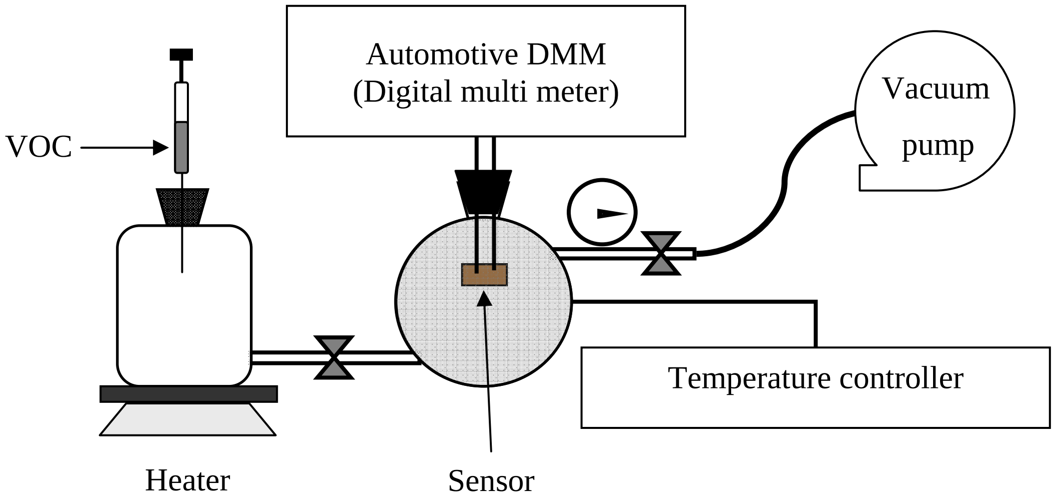

Figure 3.1 Schematic diagram of experimental apparatus for evaluating sensitivity of developed sensor

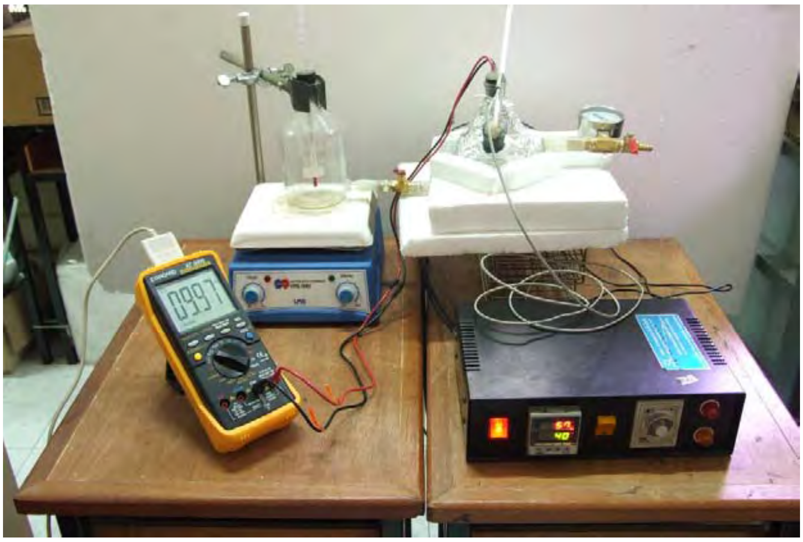

Figure 3.2 Photograph of measuring system for gas sensitivity of sensor

3.3 Experimental procedures

3.3.1 Preparation of composites polymer based gas sensor

A schematic of experimental apparatus for preparing MWCNT/PMMA composite based gas sensor was shown in Figure 3.3.

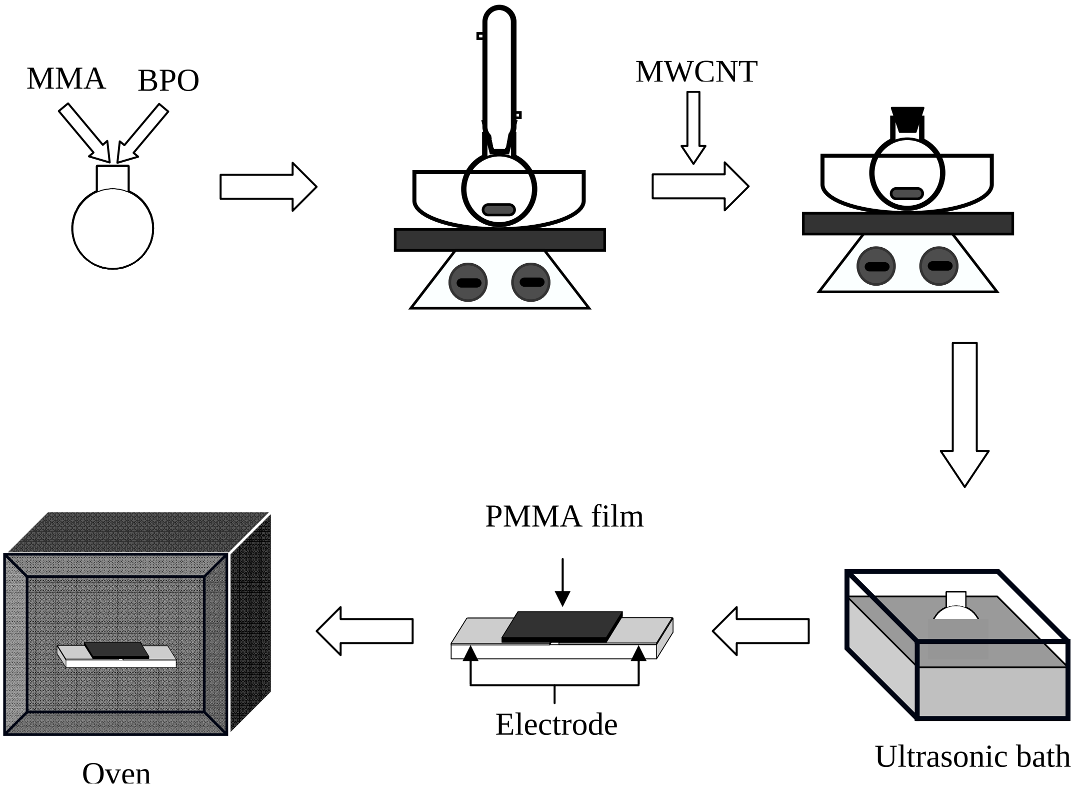

Figure 3.3 Experimental apparatus for preparing MWCNT/PMMA composite based sensor

Procedures to prepare MWCNT/PMMA composites based sensors were divided into two steps.

3.3.1.1 Fabrication of MWCNT/PMMA composites

The mixture between 5 g of MMA and 0.1 g of benzoyl peroxide (BPO) was filled in a 20 ml flask equipped with a reflux condenser and then stirred with a magnetic stirrer for a half hour at 70 °C for pre-polymerization. Then certain quantity of MWCNT, i.e. 100, 125, 150 or 175 mg, was added to the monomer and continually stirred for 5 minutes. Afterwards, the mixture was sonicated for 1 hour to yield pasty composites.

3.3.1.2 Fabrication of MWCNT/PMMA based gas sensor

A copper electrode was coated onto a plastic strip with a 1 mm gap to make a substrate for testing sensitive properties of MWCNT/PMMA composite. The composite was uniformly coated onto the electrode with the coating area of 5×5 mm and the thickness of 0.175 mm, to form composite film and put into oven at 70 °C for 48 hours to complete the polymerization.

3.3.2 Gas sensor analysis

3.3.2.1 Initial resistance of MWCNT/PMMA composite based sensor was measured by Automotive DMM with RS-232-PC interface (Figure 3.4).

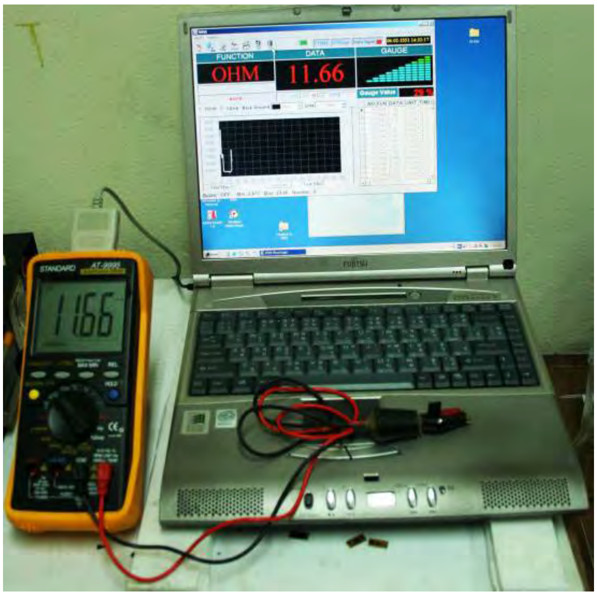

Figure 3.4 DMM (with RS-232-PC interface) connected to PC

3.3.2.2 Sensitivity measurement of MWCNT/PMMA composite based sensor

The gas sensing characteristics of the MWCNT/PMMA composite based sensor were investigated by recording its electrical resistance with respect to exposure time. Figure 3.1 was a schematic diagram of sensor assessment system in which a fabricated gas sensor was exposed to VOC gas under a controlled condition. Change of electrical reisistivity of the sensor was detected by the same DMM and input to a PC. The measurement procedure of electrical responsivity was the following

a) Vacuumed a testing chamber to -60 cmHg

b) Heated the vaporizing chamber to 140 °C. A know quantity of VOC solvent was then injected with into the flask; the solvent was immediately vaporized to gas phase.

c) Connected vaporizing chamber with testing chamber by a tube with a closed valve.

d) Opened the valve between both chambers. The pressure in testing chamber would achieve its equilibrium at -30 cmHg after being left for a period of time.

e) Opened another valve to draw diluting air into the chamber to adjust the chamber pressure to the ambient pressure.

f) Set up the sensor in the testing chamber.

g) Measured the changed of electrical resistance of the sensor with respect to the exposing time at a constant temperature.

3.4 Analytical instruments

3.4.1 Field Emission Scanning Electron Microscopy (FESEM)

The uniformity of MWCNT was characterized by Field Emission Scanning Electron Microscopy, FESEM (Figure 3.5). FESEM is a type of electron microscope that takes images of the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atom that makes up the sample producing signals that contain information about the surface topography, composition and other properties such as electrical conductivity of sample. The composite specimens were prepared by cutting the polymer plate and appropriate it onto a conductive carbon coated microscope grid. The specimens were loaded into sample chamber, and then immediately starting the observation with using image catcher scanner for taking the photos.

Figure 3.5 Field Emission Scanning Electron Microscopy JEOL, (JSM-6400)

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

A FTIR (as shown in Figure 3.6) was adopted to analyze the chemical bonding of the composite thin films. FTIR is an effective analytical tool for identification of unknowns, sample screening and profiling samples. The FTIR measuring principle is a measurement with IR light. The principle of FTIR is that the basic structure of compounds (gas/solid/liquid) can be determined by the spectral locations of their IR absorptions because specific chemical bond absorbs infrared energy at specific frequency (or wavenumber). The plot of IR transmission vs. frequency of a compound is its "fingerprint" which when compared to reference spectra identifies the material.

Figure 3.6 Fourier Transform Infrared Spectroscopy (FTIR) (model1760x)

3.4.3 Thermal gravimetric analysis (TGA)

TGA was used to analyze thermal properties of MWCNT/PMMA composite (Figure 3.7). TGA is an analytical technique used to determine thermal stability of a material and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium, Argon or N_2, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation.

Figure 3.7 Thermal gravimetric analysis (model Q600)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary study of Thermal Stability of MWCNT/PMMA Composite

In order to investigate the thermal stability of MWCNT/PMMA composite, TGA analysis was performed in a nitrogen atmosphere from 40 to 600 ºC with a constant heating rate of 10 ºC/min. The results were shown in Figure 4.1. The Figure showed that the pure PMMA and the composites began to lose weight at the same temperature, but the temperature at the maximum mass loss rate is 390 °C for composite polymer and 360 °C for pure PMMA. This preliminary indicated that

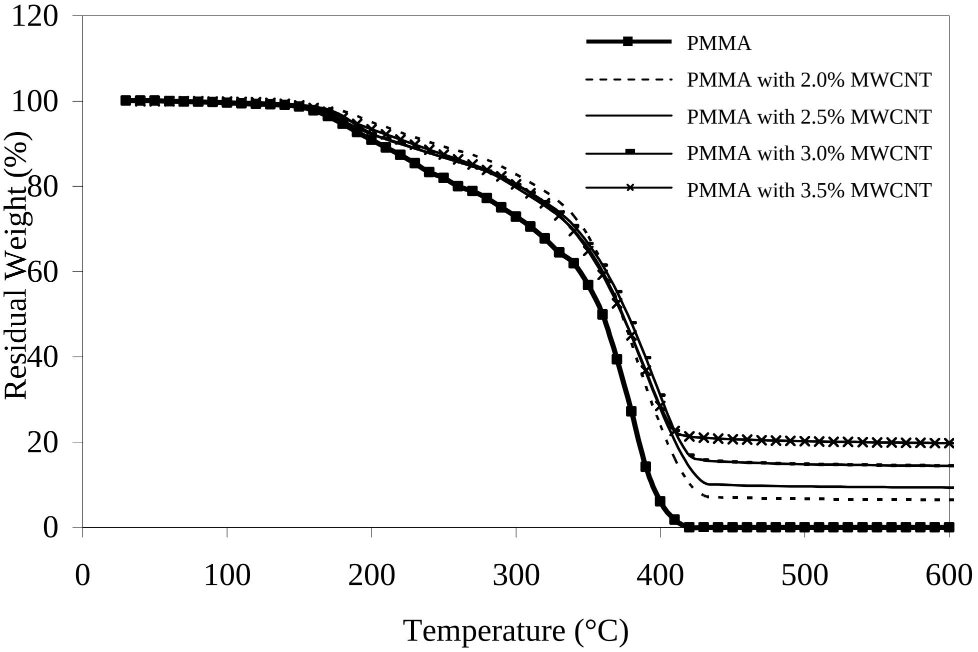

Figure 4.1 TGA analysis of MWCNT/PMMA

embedding the MWCNTs into the polymer matrix could improve the thermal stability of the polymer. It could also be noted that the MWCNTs content between 2 to 3.5 wt% used here had the same effect on improvement of thermal stability of the composite.

4.2 FTIR Spectra

Normally, molecular bonds vibrate at specific frequencies depending on the elements and types of bonding. Regarding to a specific bonding, there are several specific frequencies at which it can vibrate. IR radiation with a specific wave number range is applied to the sample. Some of the infrared radiation is absorbed, corresponding to the frequencies of vibrations between the bonds of the atoms, and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. From the abovementioned, analysis of functional groups of composites between MWCNTs and PMMA had been conducted by FTIR technique and the results were shown in Figure 4.2.

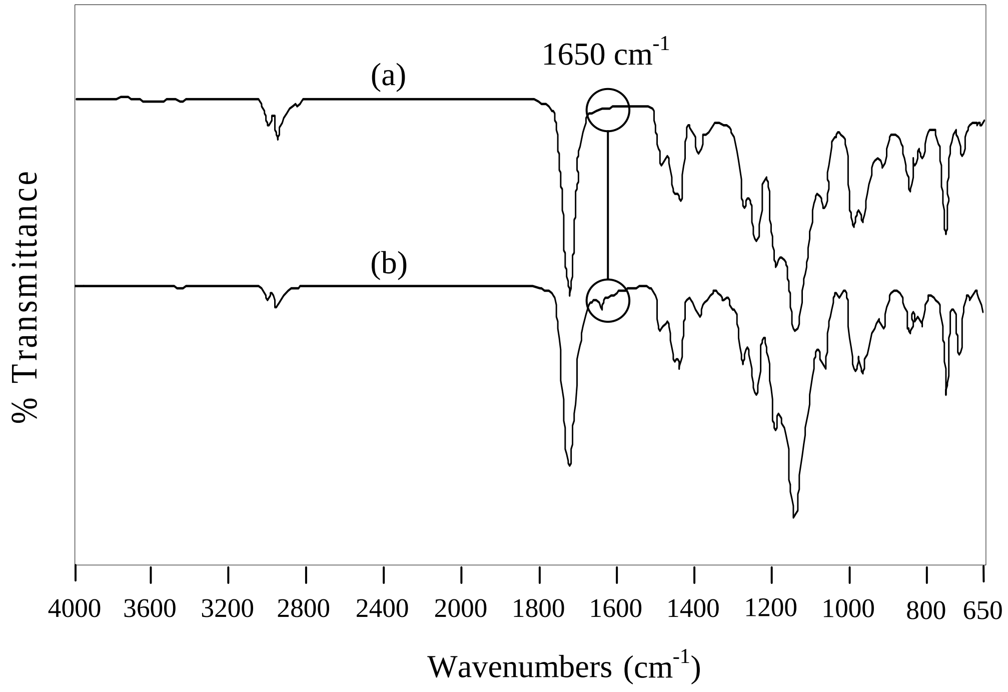

Figure 4.2 FTIR spectra of (a) pure PMMA and

(b) MWCNT/PMMA (3.5 wt% MWCNT)

FTIR spectra of MWCNT/PMMA (at3.5 wt% MWCNT) composite and pure PMMA were compared in Figure 4.2. A new peak observed in the composites at 1650 cm^{-1} originated from a C–C bond between MWCNTs and PMMA [24,26]. This result revealed that during the polymerization process MWCNTs were initiated by initiator (BPO) to open the π-bonds which can link between each other and PMMA matrix. The linking of π-bonds with opening bonds of PMMA had some effects on the polymerization process. The growth of PMMA molecules was obstructed by linkage of MWCNTs and C-C bond between MWCNTs and PMMA. Based on this result, a strong interface between MWCNTs and PMMA was produced, resulting in improvement of physical properties of the composite.

4.3 Alignment and Dispersion of MWCNT in PMMA matrix

For investigating the alignment of MWCNTs in PMMA matrix, SEM technique was adopted. Typical SEM images of MWCNT/PMMA composites were illustrated in Figure 4.3 (a)-(d). The figure showed morphology of MWCNTs dispersed in polymer matrix with weight ratio of MWCNTs to MMA of 2.0, 2.5, 3.0 and 3.5 wt%, respectively.

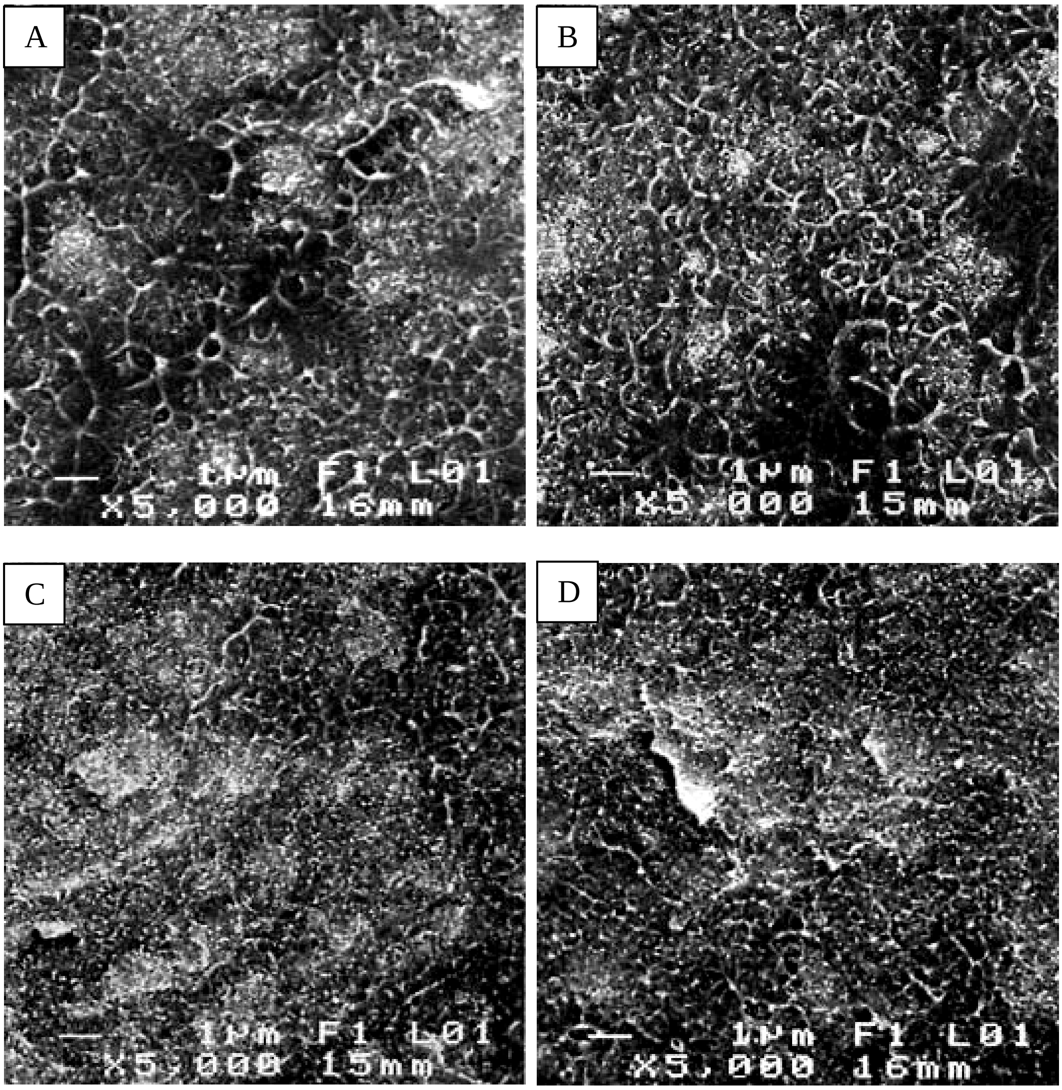

Figure 4.3 SEM Photographs of MWCNT/PMMA composites, (a) 2.0% (b) 2.5% (c) 3.0% and (d) 3.5% MWCNTs by weight

Dispersing of MWCNTs uniformly in the polymeric matrix was observed as shown in Figure 4.3. With increasing MWCNT content, network entanglement of MWCNTs became more uniform. However, when the MWCNTs wt% was higher than 3.0 wt%, the difference in MWCNT dispersion was hardly observed (Figure 4.3 (c) and (d)). From Figure the MWCNT/PMMA composite was synthesis by in-situ polymerization method. In general, PMMA is insulating materials but it might acquire certain conductivity when conductive additives such as MWCNTs were introduced. With a certain quantity of the additive enough to form the conductive path throughout the matrix, the composite resistance would decrease due to the percolation effect.

4.4 Swelling of MWCNT/PMMA composite

Effect of organic vapor on swelling of MWCNT/PMMA composite was investigated. Typical SEM images were illustrated in Figure 4.4 which compared the fresh composite and the composite which was exposed to toluene vapor at 10000 ppm for 5 minutes. From the Figure 4.4 (b), SEM image revealed a lot of holes in the polymer matrix. The hole occurred due to diffusion of vapor through the polymer and swelled the matrix. Furthermore, it should be noted that toluene is a good solvent for PMMA, hence, some parts of polymer matrix were dissolved by toluene vapor.

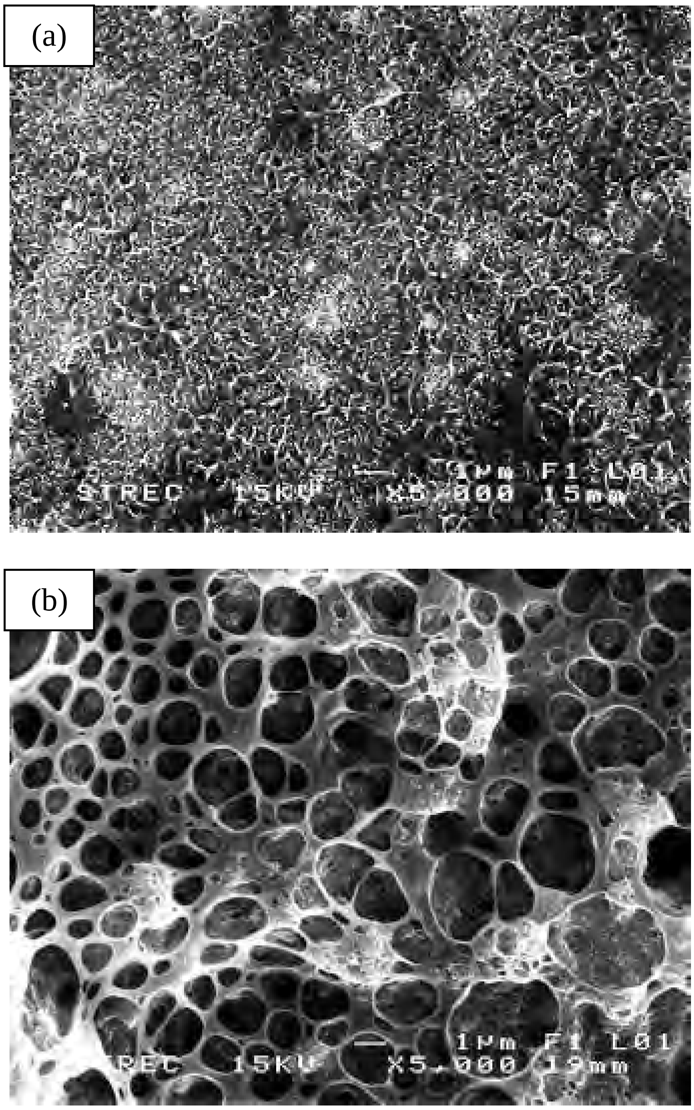

Figure 4.4 SEM images of MWCNT/PMMA polymer composites (2% MWCNT by weight) (a) virgin composite (b) composite exposed to toluene vapor at 10000 ppm for 5 minutes

4.5 Conductivity of MWCNT/PMMA composite

Generally, PMMA behaves like an electronic insulator, but many researches reported that filling of carbon nanoparticle in to the polymer matrix caused an increase in conductivity of the polymer [9]. Zhang et al. [6] revealed that the composites which were prepared by the in situ polymerization had a better dispersion of MWCNTs compared to solution mixing method. Figure 4.5 showed the relationship between resistance of the MWCNT/PMMA composites and content of MWCNTs added. It was seen that the resistance of composites was substantially decreased with increasing content of MWCNTs. According to drastic decreased of resistance with respect to MWCNTs content, it was known that the percolation threshold of the MWCNT/PMMA composites lied in about 2 wt%, the resistance of composite with MWCNT content less than 2 wt% cannot be measured. The percolation threshold had been identified as the volume fraction of conductive path that demarcates the transition from an insulative to conductive status.

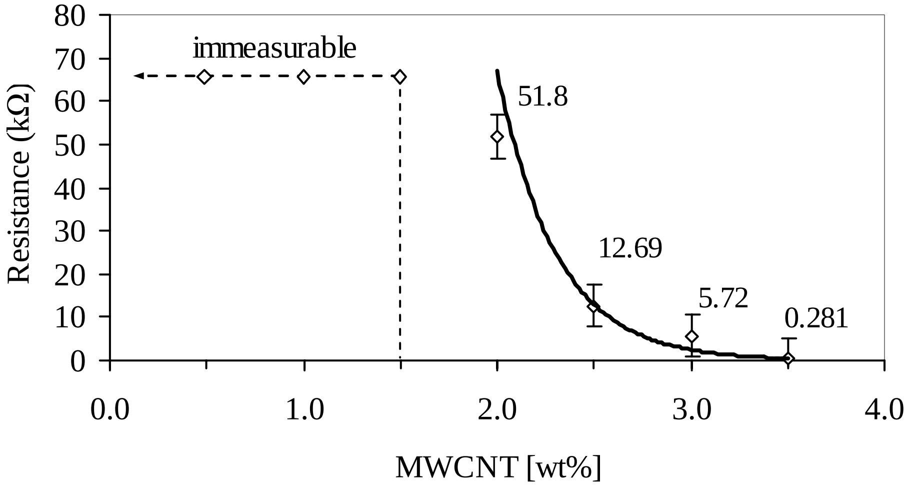

Figure 4.5 Resistance of composites polymer as a function of MWCNT content

4.6 Electrical Property characterizations and Gas Sensing

In this research, activity of MWCNT/PMMA composite based sensor had been investigated by measuring the changes of sensor electrical responsivity. The sensors were exposed to several VOC gases. Toluene, acetone, methanol and cyclohexane were used in this work. Typical change of basic resistance of MWCNT/PMMA based sensor with explosive time was illustrated in Figure 4.6. It showed an increase in the electrical resistance when the sensor of 2 wt% MWCNTs was exposed to toluene gas at 500 ppm. The resistance of the sensor became higher when the sensor was exposed to toluene for longer period.

As mentioned earlier, when MWCNT was exposed to reducing gas, electrons could be transferred form gas molecule to MWCNT, leading to formation of some positive holes on MWCNT and also an increase in electrical resistance. However, the experiment showed that although toluene is a non-reducing gas but the electrical resistance of MWCNT/PMMA based sensor was increased after the composite was exposed to toluene. This could be implied that there would be another mechanism leading to the change of electrical resistance of sensor. From investigation of other work it could be explained that the change of electrical resistance of the composite was attributable to swelling of the polymer matrix [25]. Furthermore, swelling should be a main mechanism to explain the change of resistance of MWCNT/PMMA composite based sensor. Swelling behavior of polymer relates to two parameters are permeation and polymer-solvent interaction, between gas or vapor and polymer matrix [18-21]. From all parameters permeation of vapor into a polymer is the most important.

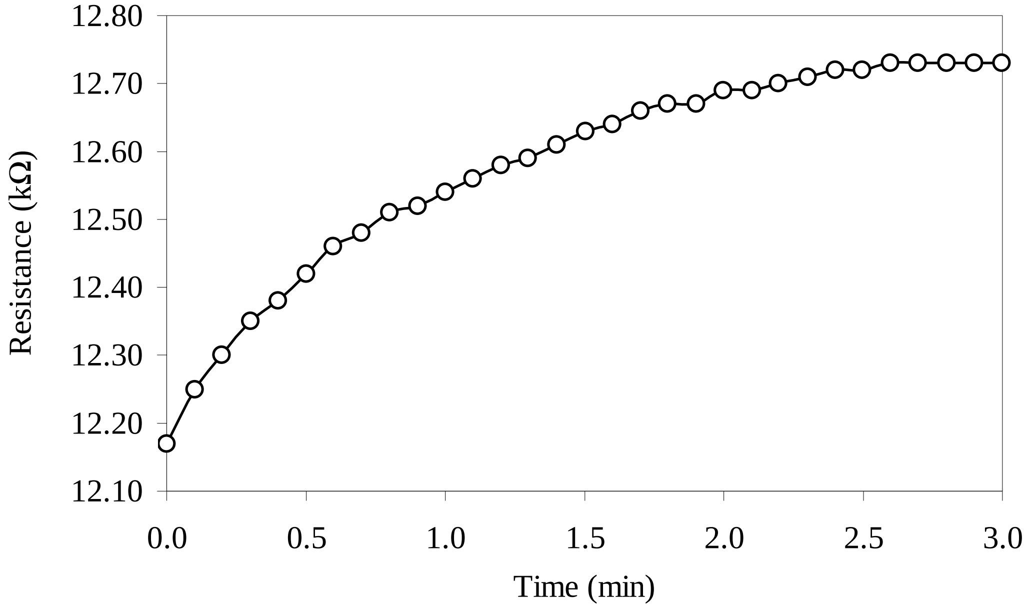

Figure 4.6 Resistance change of MWCNT/PMMA sensor with toluene exposure (2.5% MWCNTs by weight, 40 °C and 500 ppm concentrate)

Permeation is defined by the rate at which a gas passes through a polymer. The mechanism by which permeation takes place involves three steps: (a) absorption (b) diffusion and (c) desorption of a solvent from the polymer. In case of polymer which was exposed to organic gas the mechanism takes just two step, absorption and diffusion. Because diffusion of gas is a rate determining steps, then the absorption step is ignored. Diffusion of gas is connected to another property of polymer named free volume [29], a small amount of unfilled volume between polymer chains. When gas molecule diffuses into the polymer free volume it forces a rearrangement of polymer chains which leads to an increase spacing between polymer chains as shown in Figure 4.7.

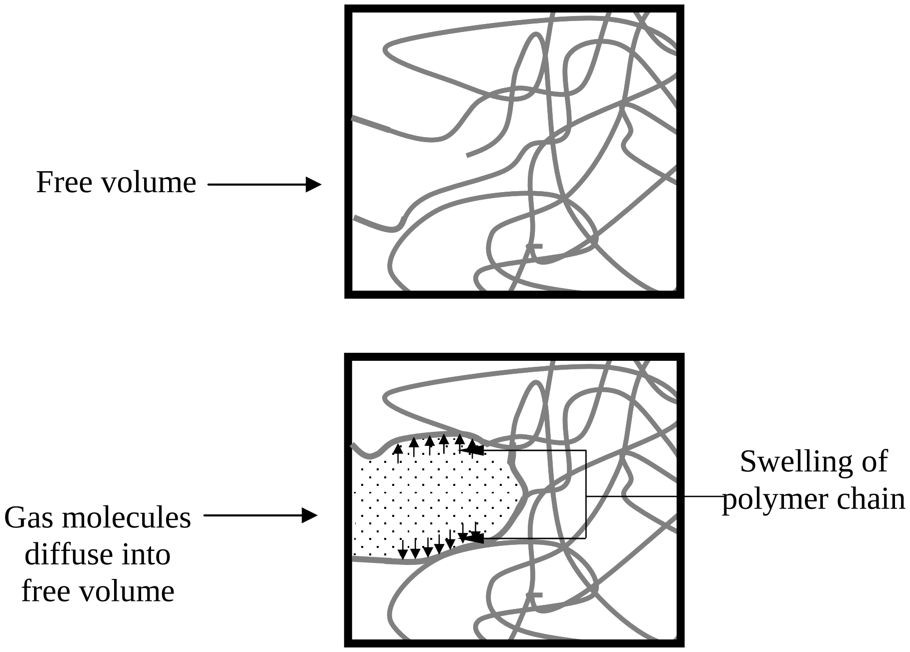

Figure 4.7 Schematic diagram of swelling of polymer chain while gas molecule diffuse into free volume

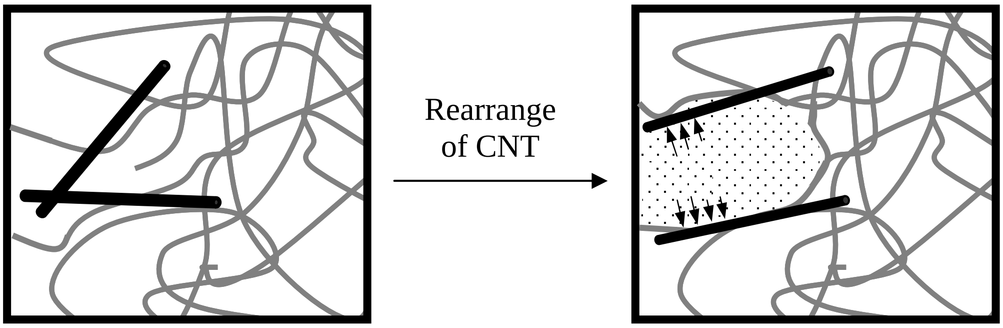

Figure 4.8 Schematic diagram of rearrangement of polymer chain and entangle MWCNTs

When MWCNT/PMMA composite based senor was exposed to VOC, the gas molecules diffused into the free volume would rearrange the polymer chain and also the MWCNTs around the polymer matrix. Thereby some gap among the entangling MWCNTs would be formed due to the volumetric expansion of the composite as shown in Figure 4.8.

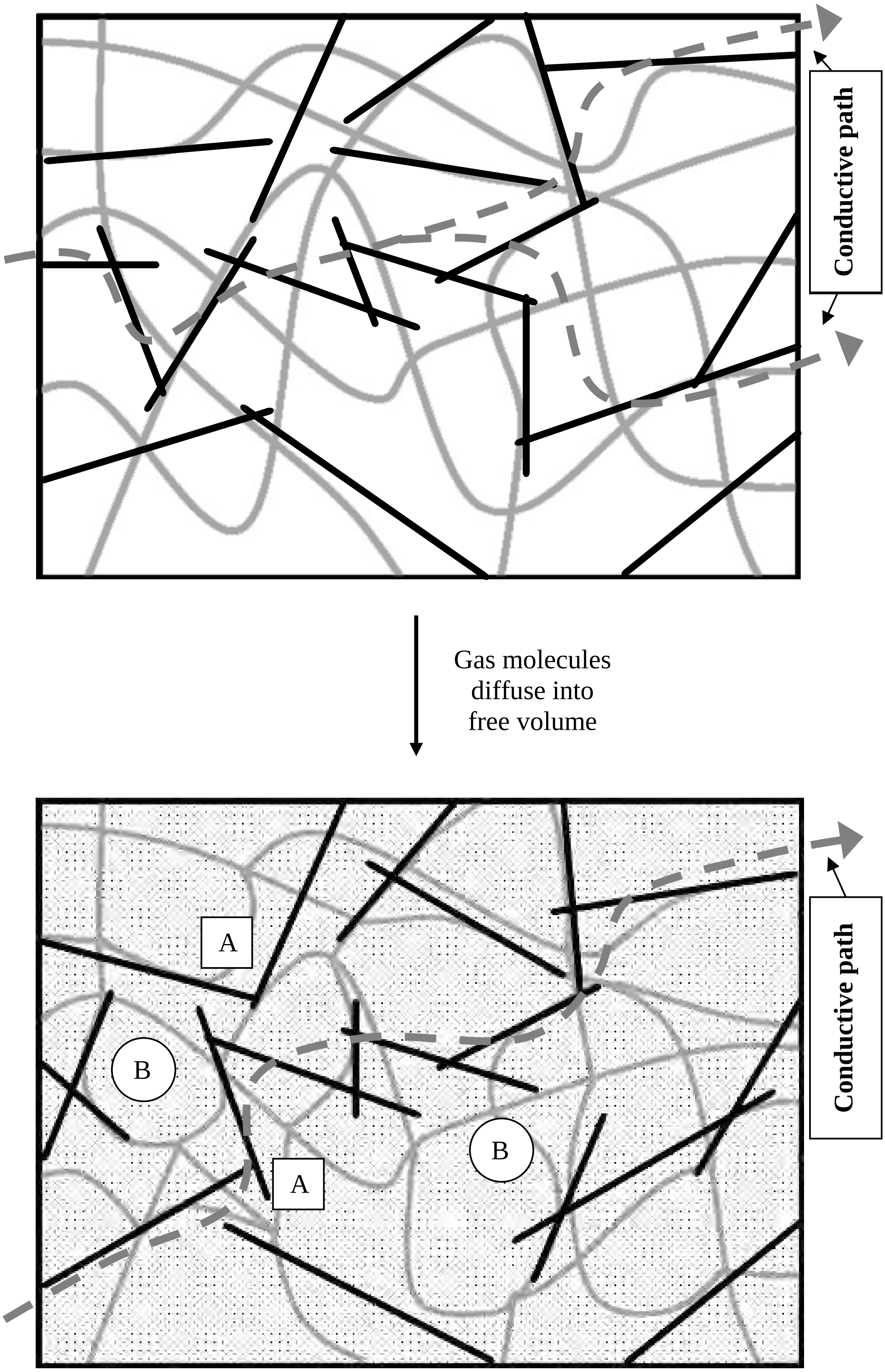

Figure 4.9 Schematic diagram of rearrangement of MWCNTs network in the composite when the polymer composite was swelled by gas molecules

Figure 4.9 showed the schematic diagram of rearrangement of MWCNTs network when gas molecule diffused into polymer free volume. As showed in the Figure, diffusion of gas molecule led to swelling of polymer chain and also rearrangement of MWCNTs. There are two possibilities which are (A) formation of new entangling path of MWCNTs and (B) breaking of MWCNT network. From Figure 4.6 the electrical resistance of MWCNT/PMMA based sensor was increased when the sensor was exposed to toluene gas. Therefore, it can be deduced that the amount of breaking of MWCNT network was larger than the amount of new entangling path of MWCNTs.

For investigation of regenerating behavior of MWCNT/PMMA composite based sensor which was exposed to VOC gas, the response and recovery curves of the sensor at operating temperature of 40 °C under toluene vapor concentration of 500 ppm were detected and shown in Figure 4.10. From the Figure, the composite sensor was exposed to toluene gas for 7 minutes after that it was exposed air for 6 minutes, and the pattern was repeated for 4 times. It was seen that the sensor exhibited a change in electrical response upon exposure to the toluene gas. Typical parameters used to determine the activity of gas sensor were sensitivity and response time.

The response, S, was defined as S (%) = $((R_t-R_0)/R_0) \times 100$, where R_0 and R_t was the resistance of the sensor at its initial and exposure states, respectively. The response time was defined as the time required for the sample resistance variation to reach 90% of peak change following a step increase in the concentration of the testing gas. In this experiment the sensor was exposed to toluene vapor until the response definitely constant, in this case it was 6 minutes. After that the sensor was removed to atmospheres, and then the response of the sensor was suddenly decreased and became constant after 4 min.

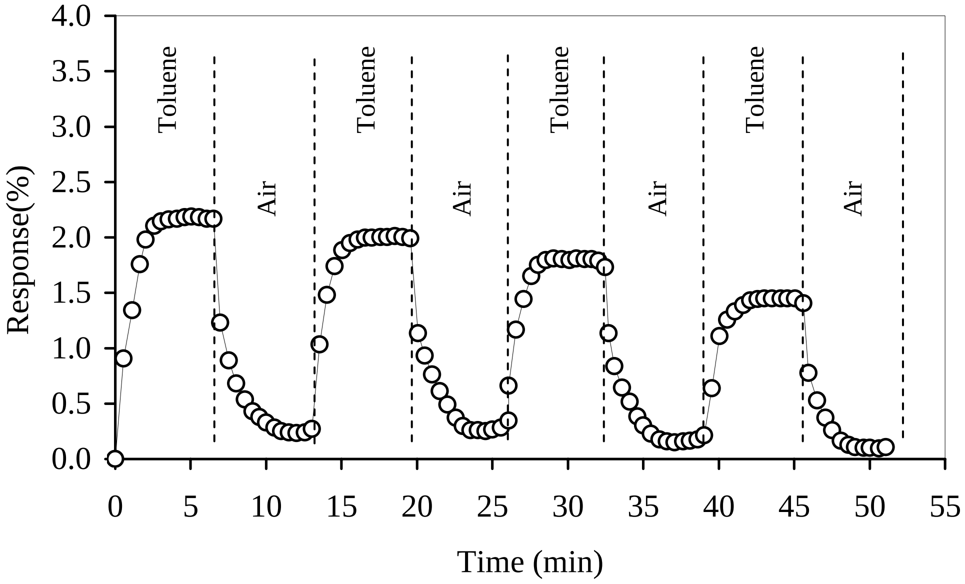

Figure 4.10 Electrical response of MWCNT/PMMA to 500 ppm concentration of toluene vapor at 40 °C (2.5% MWCNTs by weight)

In addition, the result revealed that, the composite sensor had a good response time less than 2 minutes and including a recovery behavior. As reported in the literatures that the gas sensor operating at room temperature rarely exhibits reversible response since the thermal energy is usually lower than the activation energy for desorption. This leads to a long recovery time. But for MWCNT/PMMA composite based sensor, the reversible response had been discovered at low temperature. A recovery behavior of MWCNT/PMMA sensor could be explained by mechanism of desorption. As mentioned above, gas diffusion into the polymer matrix causes the rearrangement of polymer chain. Conversely, gas desorption from polymer free volume resulted to replace of polymer chain, then the MWCNTs around that free volume returned to entanglement again.

4.7 Dependence of the Sensor Response on the MWCNTs Content

A relationship between MWCNTs content in MWCNT/PMMA composite based sensors and response of sensor was investigated by exposing sensors with MWCNTs content of 2.0, 2.5, 3.0 and 3.5 to toluene gas at 500 ppm concentration and 40 °C. A typical result was shown in Figure 4.11**.** As could be observed in the Figure, after sensors were exposed to toluene vapor for 3 minutes the response of each sensor became stable, at 6.22 4.58 2.05 and 0.96%. The composite with the lowest content of MWCNTs (2.0%) exhibited the highest response. This may suggested that the degree of entanglement of MWCNTs at high MWCNT content was higher than at low content. And the swelling of polymer by gas molecules could not reduce this entanglement effectively.

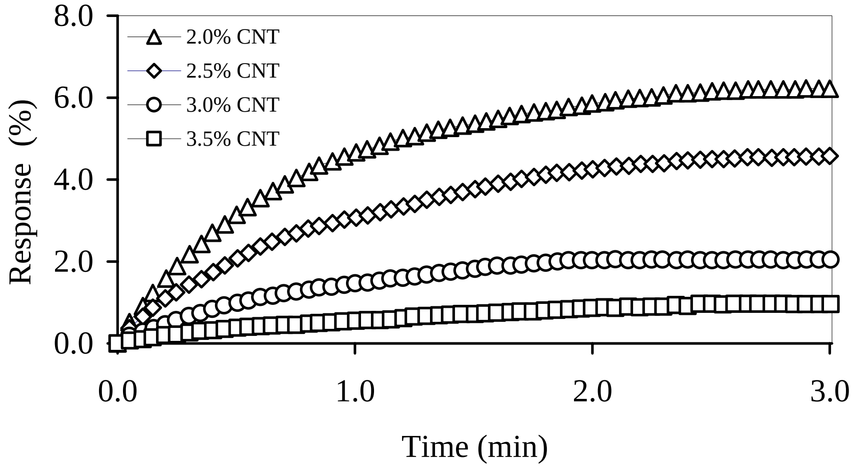

Figure 4.11 Resistance change of MWCNT/PMMA sensor in toluene exposure different content of MWCNTs (500 ppm of toluene concentration, 40 °C)

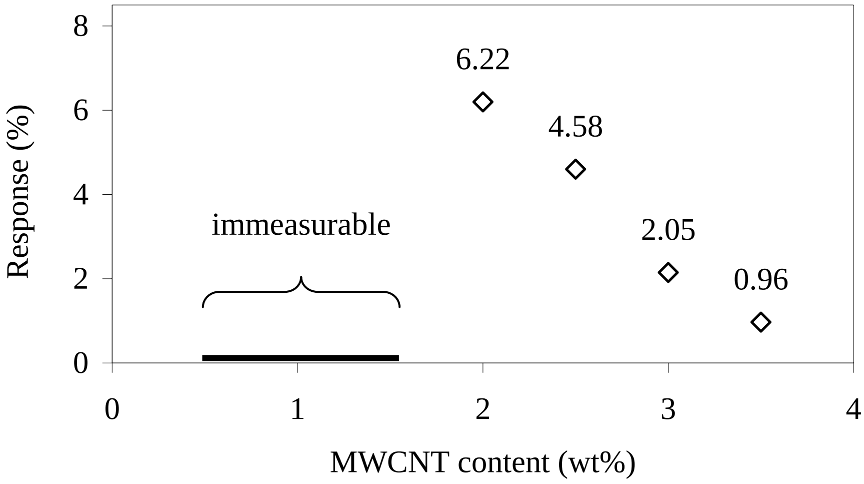

Figure 4.12 Relationship between maximum response of sensors and MWCNTs content in MWCNT/PMMA based sensor (500 ppm of toluene concentration, 40 °C)

In our investigation, the 2.0 wt% of MWCNT in MWCNT/PMMA composite was reasonably considered as the percolation threshold. Below the threshold, the composite electrical resistance became infinite, resulting in immeasurable response as shown in Figure 4.12. However, at higher MWCNT content, significant quantity of conductive path still remained even though the composite would swell after exposed to toluene.

4.8 Dependence of the Sensor Response on VOC concentration

In this section effect of gas concentration on resistance of MWCNT/PMMA base sensor was investigated. From Figure 4.13 the changes of resistance of the sensor, when exposed to toluene vapor with concentration of 500, 1000 and 1500 ppm, were illustrated. The response of the sensor increased with exposure time and became stable after certain period of time. The onset of stable response was defined as the response time of the sensor. For the toluene concentration of 500, 1000 and 15000 ppm, the response times of the sensor were 1.6 1.9 and 1.7 minutes, respectively. It can be inferred that the MWCNT/PMMA based sensor could detect toluene vapor with a concentration level as low as sub-ppm at room temperature and response of the sensor was related to concentration of the vapor (responses of sensor were 9.86 7.41 and 6.15% when the vapor concentrations were 1500, 1000 and 500 ppm, respectively).

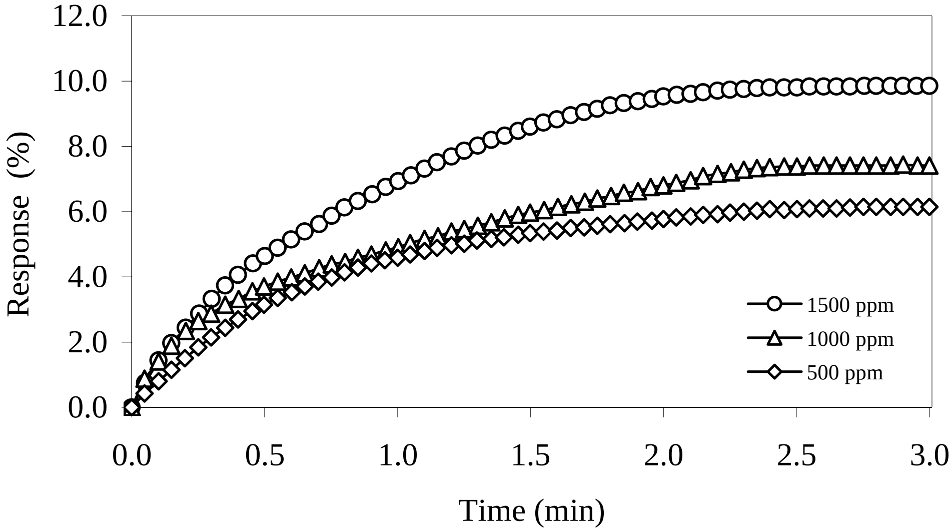

Figure 4.13 Change of resistance of MWCNT/PMMA sensor with different concentration of toluene exposed (2 % MWCNTs by weight, 40 °C)

Furthermore, it could be implied that the sensor had a fast response time to toluene vapor. The relationship between response and concentration of vapor could be explained by diffusion behavior of vapor into the polymer matrix. Diffusion of toluene vapor into the polymer was assumed to be steady state and one dimension then the basic equation governing the rate of mass transfer of toluene was defined by:

$$J = -D\frac{dc}{dz} \qquad (2.1)$$

This equation is often known as Fick’s first law. Here, J is the flux of toluene in z direction in units of moles per unit time per unit area, D (assumed constant) is the mutual or interdiffusion coefficient, c is the molar concentration of toluene. Clearly, dc/dz is the concentration gradient, and diffusion occurs due to the presence of this quantity [17]. For our work, the concentration gradient was the significant parameter which affected the flux of toluene. An increase in toluene concentration led to increased diffusion flux where as diffusion flux relates to number of molecules diffuse into polymer matrix. With larger number of molecule diffusing into the polymer matrix, higher rate of swelling occurs. It means that, higher vapor concentration gave higher swelling rate of polymer matrix; then the gaps among the entangling MWCNTs would be higher at high vapor concentration than at low vapor concentration.

4.9 Dependence of the Sensor Response on sort of VOC

Previous investigations had studied many parameters that affected the resistance change of MWCNT/PMMA sensor, such as MWCNT content and vapor concentration. However, the most interesting parameter that many researchers paid attention and tried to describe was a differential resistance change of MWCNT/PMMA in various chemical vapors. Therefore, this point was investigated in this work by fixing the weight of MWCNT at 2 wt% and the vapor concentration at 1500. After that, four different chemical vapors, such as methanol, toluene, acetone and cyclohexane, were used in this experiment. The maximum response of sensors which were exposed to each chemical vapor was illustrated in Figure 4.14. The result showed that the MWCNT/PMMA composite based sensor had high response when it was exposed to methanol vapor, and was about 12 times higher than response when exposed to toluene. Conversely, cyclohexane presented a totally different result; the response was very low.

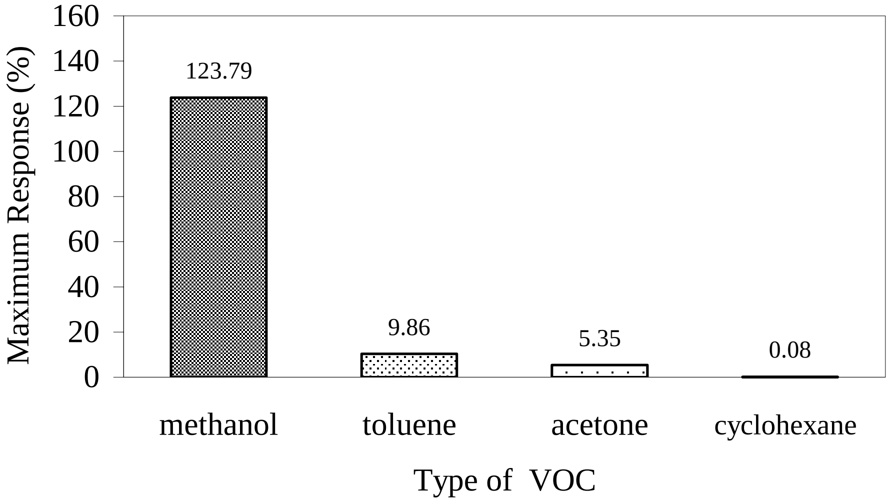

Figure 4.14 Maximum responses of MWCNT/PMMA based sensor in different organic vapor (MWCNTs content is 2% by weight, 40 °C and vapor concentration of 1500 ppm)

As discussed previously, the swelling of polymer is mainly controlled by diffusion of gas through the polymer matrix, as shown in equation (2.1). Diffusion of gas molecules is dependent on two factors which are diffusion coefficient and concentration of gas. In this section the concentrations of gases were fixed at 1500 ppm, therefore different response of sensor in different organic gases should be caused by different diffusion coefficient (D). Parameter D depends of temperature and nature of the gas/polymer system can be constant or a function of concentration. The value of parameter D normally comes from empirical and can not be estimated by particular equation. Therefore, many researchers have predicted a D value of each chemical [28]. Although the reported D values were not equivalent, but it had the same trend that the D values of attended gases use in this experiment decreased from methanol to acetone to toluene and to cyclohexane, respectively [28]. Then, degree of swelling of polymer matrix should become lower in the same direction of D and also the response of composite sensor. However, the result in Figure 4.14 showed unlike behavior of response change in toluene and acetone. From theoretical point of view the sensor which exposed to acetone should reveals higher response than sensor which exposes to toluene, because of higher D value. But the experiment resulted in the opposite behavior. It suggested that, salvation of polymer might be another parameter that affected the response of the sensor [25].

Solvation of polymer in solvent is a part of theory of polymer solution that explains an interaction between polymer and solvent. In case that polymer dissolves in organic solvent, the polymer dissolution was explained by solvent diffusion. The steps of solvent diffusion include salvation and swelling, gel formation and net work polymer stopped. But for gas diffusion into the polymer matrix the concentration of organic molecules are poor. Therefore, the diffusion step covers only solvation and swelling, gas molecules destroy some part of polymer matrix cause to changing of response of sensor. However, some reasons can be applied to explain the behavior of polymer and organic vapor interaction. As a rule “like dissolve like” if the bonds in polymer chains and in the chemical molecules are similar in polarity, then the energy of interaction between homogeneous and heterogeneous molecules is nearly identical

[29]. In general, a polymer matrix has specific interaction with chemical molecules. If polymer and vapor molecules differ greatly in polarity, the polymer matrix has not interacted with the vapor. Chemicals which used in this experiment were divided to three groups as shown in Table 4.1.

Table 4.1 Polarity of chemicals [30]

High polarity	Average polarity	Non polarity
Methanol	Toluene & Acetone	Cyclohexane

Because PMMA is an average polarity polymer then toluene and acetone have a drastically interact to PMMA matrix and make them destroyed, cause to high response of the sensor.

Interaction between polymer matrix and each chemical vapor, toluene and acetone, was compared by polymer-solvent interaction parameter (χ).where χ is a dimensionless use to predict the miscibility of polymer and solvent, is defined by [20]

$$\chi_{12} = \frac{V}{RT}\left[(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2\right] + \beta \qquad (2.2)$$

Where V is the molar volume of the solvent, δ is the solubility parameter for the solvent (1) and polymer (2) while δ_D, δ_P and δ_H Hansen solubility parameters for dispersion, polar and hydrogen bonding interaction, respectively. R is the gas constant and T is the absolute temperature. The empirical constant β is usually taken to be constant at 0.34. For a polymer which would be dissolved in a solvent at a particular temperature, χ would be below 0.5. In case of acetone and toluene χ has been empirical predicted, the average value are 4.8 and 4.5, respectively [31]. As a lower χ of toluene the polymer matrix was much destroyed than acetone, cause to high changing of response of the sensor. In case of methanol and chyclohexane χ is higher than 0.5, then the polymer matrix was supposed to be not destroyed.

CHAPTER V

CONCLUSIONS

5.1 Analysis of MWCNT/PMMA composite

With sonicated mixing, conductive composites could be prepared by the in-situ polymerization of MMA with MWCNTs. Based on the analysis of the composite properties it was found that embedding the MWCNTs into the polymer matrix could improve the thermal stability of the polymer composite. During polymerization process, the growth of PMMA molecules was affected by entangling MWCNTs and C-C bond between MWCNTs and PMMA, leading to improvement of thermal properties of the composite. By comparison of SEM image of composite polymer, it was found that with increasing of MWCNTs content, network of entangling MWCNTs became more uniform. After being exposed to toluene vapor, the swelling of the polymer matrix could be confirmed by SEM analysis.

5.2 Analysis of MWCNT/PMMA composite based sensor

MWCNT/PMMA composite based sensors were fabricated by a screen printing method. Based on results, the composite sensor showed the relationship between MWCNTs content and initial electrical resistance of sensor. The electrical resistance of the composites was substantially decreased by the increasing content of

MWCNTs. Furthermore, the percolation threshold of the MWCNT/PMMA composites was found at 2 wt% of MWCNTs. The activity of composite sensor was investigated and found that when the composite was exposed to toluene or other organic compounds, polymer matrix would swell, resulting in a destruction of conductive path. Thereby an increase in electrical resistance of the sensor could be observed. Furthermore, the experimental results revealed that with the lowest MWCNTs content of 2wt%, degree of swelling in the composite matrix became much higher. Therefore, the electrical resistance of the composite with the lowest MWCNTs content changed substantially. In addition, the experiment showed that the response of sensor was increased with an increase in toluene concentration. The higher diffusion flux could result in the higher degree of swelling of polymer matrix. Finally, type of VOC also significantly affected the response of the fabricated sensor. This result was attributed to two parameters, which were diffusion of vapor into polymer matrix and polymer-solvent interaction. In this work the sequence of response could be achieved when the sensor was exposed to methanol, toluene, acetone and cyclohexane, respectively.

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APPENDICES

Conference and Publications

From This Research Work

CONFERENCE

International Proceedings

Amornwong Srisurichan, Adi Ilcham, Apinan Soottitantawat, Yongyuth Wanna and Tawatchai Charinpanitkul. “Poly Methyl Methacrylate-Multiwalled Carbon Nanotubes Composites for Detecting Volatile Toluene Gas” *Proceedings of international symposium on Pure and Applied Chemistry International Conference (PACCON 2008), January 30- February 1, 2008, Thailand.*

PUBLICATION

This paper was published in the Kasertsart University Science Journal (KUSJ) Vol. 26, No. 1, Jan-Apr 2008.

POLYMETHYL METHACRYLATE-MULTIWALLED CARBON NANOTUBE COMPOSITE FOR DETECTING VOLATILE TOLUENE GAS

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Abstract

Nowadays, air pollutions have been a chronic problem in various countries including Thailand. Contamination which is related to volatile organic compounds emitted from many industrial settlements could result in negative effect on public health of surrounding community. Therefore, a requirement of those toxic gases detection has became an urgent issue for many scientists and researchers to challenge. Meanwhile, in an aspect of new material, one of the most cited materials is carbon nanotube due to its promising properties such as high surface area and sensitivity to some specific gas. In this research, a composite of polymethyl methacrylate (PMMA) and carbon nanotube (CNT) which is fabricated by the in situ polymerization method has been investigated. As primary experimental results, original sensors fabricated from composites of PMMA and CNT with CNT weight ratio of 2.0, 2.5, 3.0 and 3.5 were employed to detect toluene as a simulated pollutant gas. Regarding to the CNT content, the fabricated sensor could provide 51.80, 12.69, 5.72, 0.32 kΩ, respectively. The sensitivity within a range of 5% with toluene concentration of 500 ppm, and response time less than 2 minutes of the sensors was experimentally investigated.

Keywords: conductive polymer, gas sensor, composite

1. Introduction

Since its discovery in 1991[1], CNT has drawn attentions from many parts of science and engineering due to its unusual physical and chemical properties. Because of outstanding properties, such as mechanical, thermal and electronic properties, CNT is expected to use as advanced filler materials in composites. CNT has become as ideal candidates for nanoscale sensor devices, owing to its high surface areas that provide by 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 [2-5].

Because CNT is an excellent material to apply for gas detection many investigations of composite between CNT and other materials have been conducted by many researches, particularly for improvement of gas detection efficiency [6-8]. In this research, one of very interesting polymer, PMMA, is selected as the matrix polymer while CNT as a filler. 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 could swell when VOC molecules are absorbed into the matrix. [7]

Among various pollutant gases, toluene was chosen as a target gas because it could swell. Toluene 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.

2. Experimental

2.1 Materials

Multi-walled carbon nanotubes were obtained from Bayer Material Science 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 supplied by Thai MMA 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 filled in a 20 ml flask equipped with a reflux condenser and then stirred with a magnetic stirrer for a half hour at 70°C for pre-polymerization. Then certain quantity of CNT, 100, 125, 150 and 175 mg, was added to the monomer. Afterwards, the mixture was sonicated for 1 hour to yield pasty composites [9]. Uniformity of the blended composite was visually observed before taken to analyze by electron microscopy.

2.2.2 Fabrication of PMMA/CNT base gas sensor

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

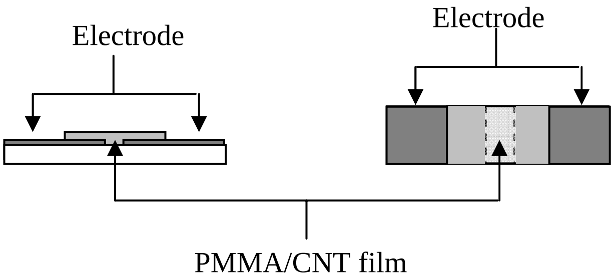

Figure 1 Structure of sensor

2.2.3 Measurement

Typical scanning electron microscope (SEM) images of the CNT/PMMA composites film were obtained by a field emission SEM instrument (JEOL, JSM-6400). The initial resistivity of each sensor was measured by Automotive DDM (with TS-232-PC interface). The gas sensing characteristics of the CNT/PMMA were investigated by recording its electrical resistivities with respect to exposure time. **Fig. 2** is 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.

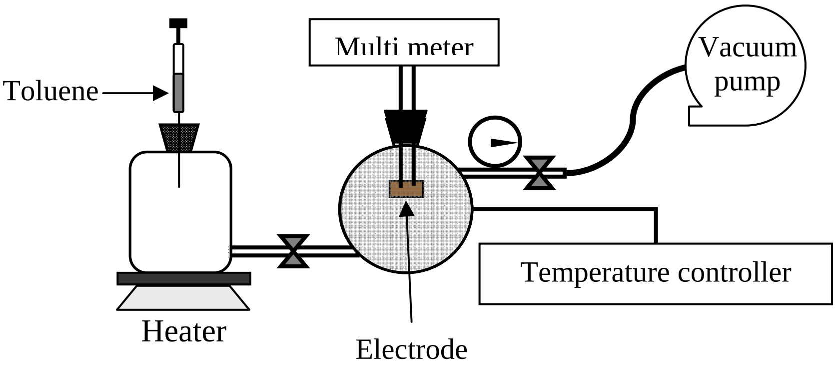

Figure 2 Measuring system for gas sensitivity of sensor

The measurement procedure of electrical responsivity was started by heating the left flask to 140°C and toluene was injected with a known quantity 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 exposing time at a constant temperature of 40°C

3. Results and discussion

Typical SEM images of CNT/PMMA composites were illustrated in **Figs. 3(a)-(d)** and then analyzed for comparison of CNT dispersion in matrix with weight ratio of CNT to MMA of 2.0, 2.5, 3.0 and 3.5 wt%, respectively. MWCNT dispersing in the polymeric matrix could be observed as light stripes scattering on the dark background. 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 (**Figs. 3 (c**) and **(d)**). This method to prepare such composite is known as in-situ polymerization. PMMA is insulating materials but it might acquire certain conductivity when conductive additives are introduced. With a certain quantity of the additive enough to form the conductive path throughout the matrix, the composite resistivity would decrease due to the percolation effect. **Fig. 4** shows the relationship between resistivity of the CNT/PMMA composites and content of MWCNT added. It is seen that the resistivity of composites substantially decreased by the increasing content of CNT.

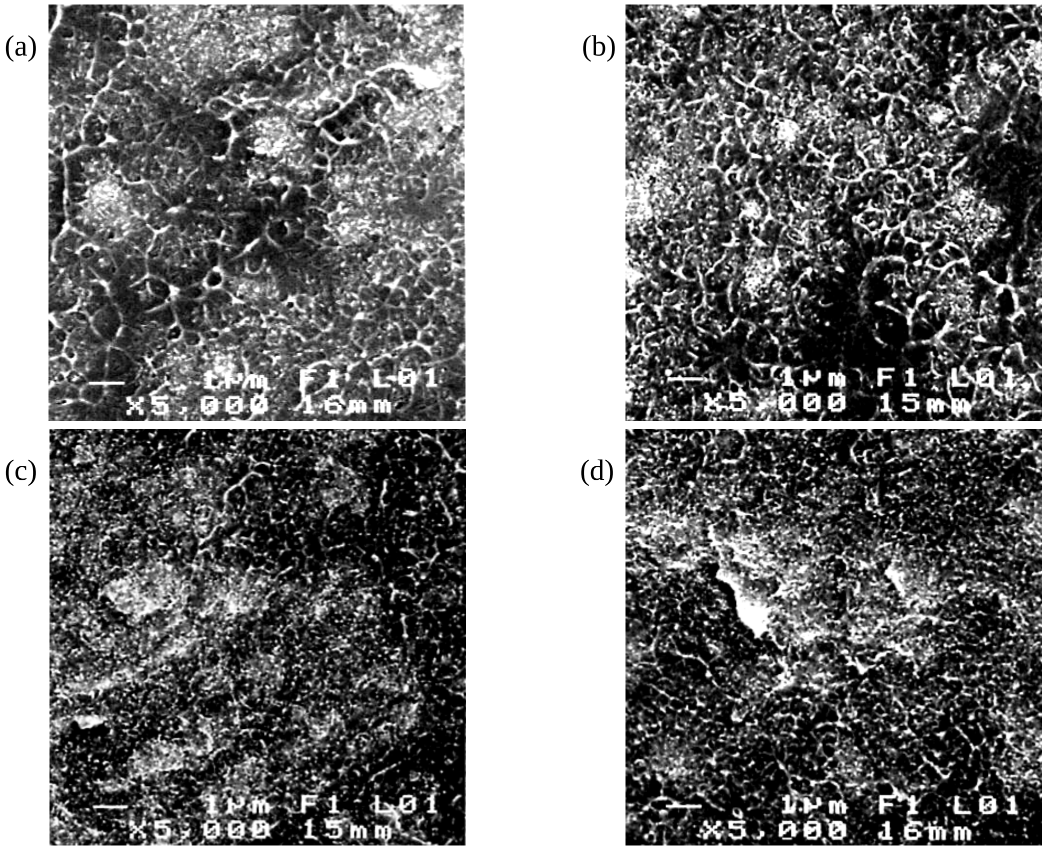

Figure 3 SEM Photographs of CNT/PMMA composites, (a) 2.0% (b) 2.5% (c) 3.0% and (d) 3.5% CNT by weight MMA

Electrical responsivity of CNT/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 [8]. 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 [6-8].

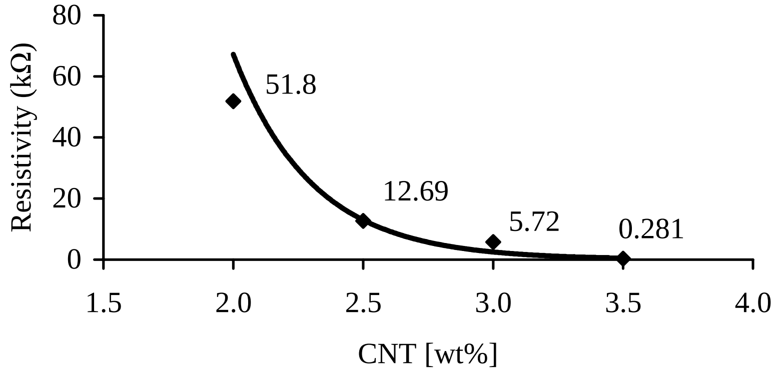

Figure 4 Resistivity of composites polymer as a function of CNT content

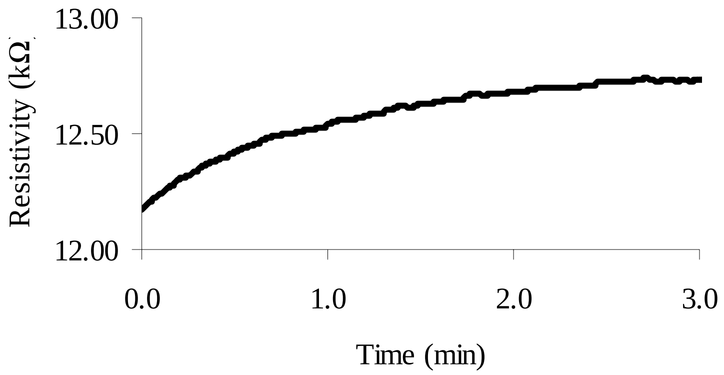

Figure 5 Resistivtiy change of PMMA/CNT sensor with toluene exposure (2.5% CNT by weight MMA, 40 °C and 500 ppm concentrate)

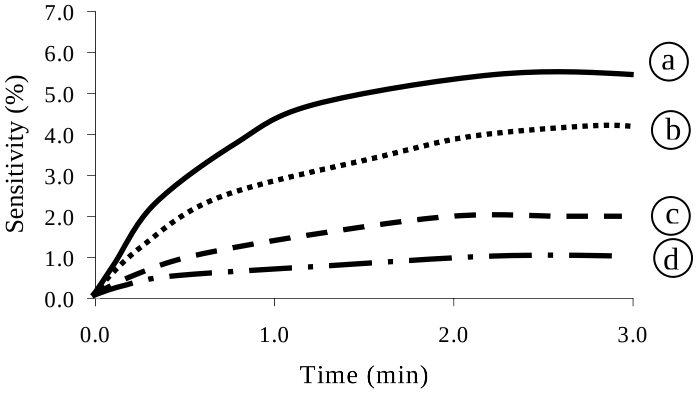

Figure 6 Comparable of resisitivity change of PMMA/CNT in toluene vapor (40 °C and 500 ppm concentrate) when a, b, c, and d is 2.0, 2.5, 3.0 and 3.5% CNT by weight MMA

The electrical responsivity of different content of MWCNT in the composites was experimentally investigated. The sensitivity, *S* was defined as S (%) = $((R_t-R_0)/R_0) \times 100$, where R_0

and R_t are the resisitivity of the sensor at its initial and exposure states, respectively [7]. 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 unsidered as the percolation threshold. Below the threshold, the composite electrical resistivity became infinite, resulting in immeasurable sensitivity. However, with a higher MWCNT content, significant quantity of conductive path still remained even though the composite would swell after exposed to toluene. Further 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.

4. Conclusion

By a mean of sonicated mixing, conductive composites could be prepared by the in-situ polymerization of MMA with MWCNT. With increasing MWCNT content, the conductive path became more uniform, leading to the lower electrical resistivity of the composites. When the composite was exposed to toluene vapor, polymer matrix would swell, resulting in a destruction of conductive path, leading to an increase in 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.

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