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THESIS

MODIFICATIN OF POLY(VINYL ALCOHOL) BY SIMPLE ORGANIC REACTIONS FOR USING AS ELECTRONIC NOSE MATERIALS

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A Thesis Submitted in Partial Fulfillment of
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Modification of poly(vinyl alcohol) by esterification is one of alternative ways to prepare copolymers. The degree of esterification on PVA was determined by FTIR, ^{1}H-NMR, and elemental analysis. The chemical vapour sensors were fabricated by mixing polymer and carbon black in DMSO afterwards prepared as thin films onto the interdigited electrodes (IDE) by spin-coating technique. To investigate the chemical vapour sensing property, the chemical sensors were examined with various organic solvents such as hexane, toluene, alcohols, THF, ethyl acetate, etc. The experimental results indicated that the composites have various responses to various solvent vapours.

Keywords: PVA modification, chemical vapour sensor, carbon black composite

Student's signature Thesis Advisor's signature ___ / ___ / ___

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LIST OF ABBREVIATIONS

PVA = poly(vinyl alcohol)
R- = alkyl or aryl group
CB = carbon black
^{o}C = degree celcius
cal = calorie
MHz = megahertz
ppm = part per million
δ = chemical shift
s = seconds
min = minutes
h = hour
σ = electrical conductance
mL. = milliliter
g = grams
mmol = millimole
M = molar
% = percentage
nm = nanometer
cm^{-1} = per centimeter
mS = milisiemens
Ω = ohm
Da = dalton
rpm = rounds per minutes

MODIFICATION OF POLY(VINYL ALCOHOL) BY SIMPLE ORGANIC REACTIONS FOR USING AS ELECTRONIC NOSE MATERIALS

INTRODUCTION

Organic solvents are widely used in a large number of industries and laboratories. Most organic vapours are, however, dangerous and toxic to human health. Breathing it for long periods may cause nerve, kidney, and liver damage. The vapours of some solvents such as hexane and toluene are flammable. In addition, tetrahydrofuran is able to form highly explosive organic peroxides upon exposure to oxygen and light. It indicates that the organic vapours contaminating in the ambient air may cause dangerous. Developing and designing sensors for the specific detection of hazardous components in their mixtures has been, therefore, focused.

Up to now, an electronic nose which imitates the mammalian olfactory system has been still attractive to many researchers for application of chemical sensor. An electronic nose generally consists of an array of sensitive chemical sensors and an appropriate pattern recognition process in order to detect and discriminate the complicated analytes or the odours. The sensitive chemical sensor might be prepared from metal oxide semiconductor (MOS), quartz crystal microbalance (QCM), surface acoustic wave (SAW), conducting polymer (CP), and composite of non-conducting polymer.

Nowadays, the sensitive chemical sensors made from composite between non-conducting polymer and carbon black have received significant attention for use in detecting and discriminating among various organic vapours in laboratory or environmental monitoring. The composites consisting of insulating polymer and carbon black exhibit many advantages, such as, ease of manufacturing, reasonable cost, various polymers used, and various analysts detected. The mechanism of electrical responsibility can be described on the basis of percolation theory. During exposing to the analytes, the polymer matrix of the composites was swollen or shrunk causing a change in the conductive pathway within the composite film.

By using the basic of composite between non-conducting polymer and carbon black, in this work, poly(vinyl alcohol) (PVA) was modified by simple reaction as esterification before compositing with carbon black. The unmodified and modified PVA with different in chemical structures and polarities were investigated on their vapour sensing behaviours in various solvent vapours.

OBJECTIVES

1. Modify the poly(vinyl alcohol) structures by esterification reaction for using as organic vapour sensing material.

2. Study on the sensing property of esterified poly(vinyl alcohol) for organic vapours.

LITERATURE REVIEW

Poly(vinyl alcohol)

Poly(vinyl alcohol) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing poly(vinyl acetate) in ethanol with potassium hydroxide. In commercial, poly(vinyl alcohol) can be produced from poly(vinyl acetate) by a continuous process. Generally, poly(vinyl alcohol) is treated with methanol and a small amount of base like sodium methoxide as catalyst. The acetate groups are hydrolyzed by ester interchange with methanol. Poly(vinyl alcohol) is, therefore, classified into two classes namely: partially hydrolyzed and fully hydrolyzed.

Poly(vinyl alcohol) cannot be prepared from its monomer similar to other vinyl monomers because an acetaldehyde form (keto tautomer form) is more stable than a vinyl alcohol form.

$$H_2C=CH(OH) \rightleftharpoons H_3C-CH=O$$

The physical characteristics of poly(vinyl alcohol) are dependent on its preparation methods, such as, from the hydrolysis or partial hydrolysis, of poly(vinyl acetate). Poly(vinyl alcohol) is, therefore, classified into two groups, partially hydrolyzed and fully hydrolyzed.

Because of a plenty of hydroxyl groups on the structure of poly(vinyl alcohol), it has been often used as the starting materials for various reactions, such as, esterification, transesterification and etherification. In addition, it has been also applied in a wide range of industrial, medical and food applications.

Zee's research indicated that the structural change of polymer affect responsibility of sensor. In this work, the poly(vinyl alcohol) was modified to preliminary study correlation between the vapour sensing property and structure transformed.

Zee *et al.* (2001) studied six polymer-carbon black composite film were deposited into the sensor array and exposed to three chemical gases at five different concentration levels. The sensors were able to uniquely detect these gas vapours and demonstrated a linear response to concentration levels between 2000 and 10,000 ppm. This design allows the integration of circuits to process the changes in resistance which will permit the realization of a completely integrated miniature gas sensor.

Esterification reaction

Esterification is the chemical reaction used for preparing ester compounds. The general structure of esters is R-COO-R', where R and R' are either alkyl or aryl groups. Generally, esters are prepared by the reaction of carboxylic acid and alcohols by using the mineral acid as a catalyst. However, the other reactive acids, such as, acid chloride (R-CO-Cl) and anhydride (R-CO-O-CO-R') can be used instead of the carboxylic acids.

Spin coating technique

Spin coating technique as shown in Figure 1, involving the depositing a thin layer of a polymer solution onto a substrate, has been widely used for the thin film applications. Spinning a substrate at high spin speed, the centrifugal force will cause the polymer solution spreads to the edge of the substrate resulting in a thin film of polymer on the surface of the substrate.

Two common methods of dispense are Static dispense and Dynamic dispense. Static dispense is simply depositing a small puddle of fluid on or near the center of the substrate. This can range from 1 to 10 cc depending on the viscosity of the fluid and the size of the substrate to be coated. Higher viscosity and or larger substrates typically require a larger puddle to ensure full coverage of the substrate during the high speed spin step. Dynamic dispense is the process of dispensing while the substrate is turning at low speed. A speed of about 500 rpm is commonly used during this step of the process. This serves to spread the fluid over the substrate and can result in less waste of resin material since it is usually not necessary to deposit as much to wet the entire surface of the substrate. This is a particularly advantageous method when the fluid or substrate itself has poor wetting abilities and can eliminate voids that may otherwise form.

After the dispense step it is common to accelerate to a relatively high speed to thin the fluid to near its final desired thickness. Typical spin speeds for this step range from 1500-6000 rpm, again depending on the properties of the fluid as well as the substrate. This step can take from 10 seconds to several minutes. The combination of spin speed and time selected for this step will generally define the final film thickness.

Main factors affected to thickness of film are the nature of polymers, such as, viscosity, drying rate, surface tension, and etc. The other factors are the spin process conditions, such as, spin speed, acceleration, spin time, and etc.

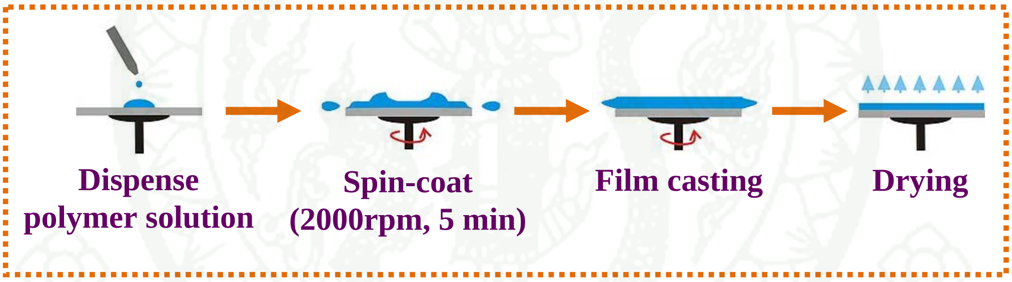


Figure 1 Schematic view of the spin coating technique.

Polymer using as sensing materials

A polymer using as sensing materials has two types i.e. conducting polymer and polymer composite. A conducting polymer has electrical and optical property like metal of semiconductor but still exhibits individual mechanical property of polymer. The past three decades, the polymer property was seen as insulator only. Therefore, it is often used as inert a packaging. Afterwards, Heeger *et al.*discovered a conducting polymer; polyacetylene. Up to now, conductive polymer has widely application such as light emitting diodes, solar cell, and transistor. Moreover, the conducting polymer was used as material in various type of sensors including electronic nose.

Barisci *et al.* (2002) studied the possibility of detecting volatile aromatic hydrocarbons using the concept of an electronic nose. An array of sensors based on polypyrrole polymers has been used to identify and quantify the benzene, toluene, ethyl benzene, xylene (BTEX) compounds. A number of dopants have been investigated in terms of their ability to form suitable electrochemically deposited polymer films and to detect the analyte gases with sufficient sensitivity and reproducibility. A group of eight polymers has been found to meet most of the requirements for this application.

Radhakrishnan *et al.* (2007) studied polypyrrole (PPy) modified with ferrocene (Fc) by direct incorporation during polymerization so as to increase its sensitivity for carbon monoxide (CO) gas sensor applications. Synthesis was carried out by chemical oxidative polymerization in the presence of ferrocene using ferric chloride. The CO response measurements were carried out for the sensors fabricated in a surface cell mode with active PPy + Fc films by exposing to CO gas (300 ppm) at room temperature and it was found that the response as well as the recovery characteristics of these materials is very fast and dependent on the film composition. The response factor was found to be maximum for a 1.32 mol% Fc content in the polymer. These various results can be explained on the basis of interaction of CO molecules with Fe atoms of the ferrocene together with charge transfer interaction with the PPy chain.

However, the conducting polymer is more expensive and not diversity. The non-conducting polymer is, therefore, replaced conducting polymer. In order to increase the electrical property, the non-conducting polymer is added metal or carbon black as composite material.

Dong *et al.* (2004) studied electrical resistance responses of amorphous polymer composites against various organic vapors at low concentrations by using polymerization-filling fabricated carbon black/poly(butyl methacrylate) (CB/PBMA) system as the model material. The experimental results indicate that the composites have high selectivity to various organic vapors at the same concentration. In addition, the electric resistance response of the composites against organic vapors takes place in step with their vapor adsorption procedure. It is demonstrated that uptake of solvent vapors in the matrix polymer guarantees the increase in a composite's resistance over a wide range of vapor concentration. According to these findings, the composites can be used as an organic vapor sensor to detect, quantify and discriminate various organic vapors. Unlike the case of saturated vapors, similarity between the solubility parameters of the matrix polymer and a solvent can no longer serve as a criterion to predict the response of the composite against the low concentration solvent gas.

Lei *et al.* (2004) studied chemiresistor sensors comprised of conductive polymer composites identifying gaseous analytes. The performance of these sensors depends on a number of parameters, including the geometry and concentration of the conductive component dispersed in the polymer. In this study, 64 chemiresistors representing eight different carbon concentrations (8–60 vol.% carbon) were constructed by depositing thin films of a carbon black–polyisobutylene composite onto concentric spiral platinum electrodes on a silicon chip. The impact of carbon concentration and geometry on the measured resistance and derived resistivity of the polymer composite was determined.

Electronic noses

Electronic nose is an instrument that has been developed to mimic the olfactory system of human and used for many applications from identifying solvents to natural products. This device consists of an array of electronic chemical sensors with partial overlapping sensitive materials to classify analyzes and an appropriate pattern recognition system capable of recognizing simple or complex odours. The volatile compounds react with the sensors, both in the electronic and mammalian noses, to generate an electronic signal which was pre-processed and amplified, before being sent to a recognition organ, either the brain or a computer. However, the operating principles including the sensitivity and selectivity are very different. It was the fact that the sensitivity of the human nose is undoubtedly far superior to that of any electronic equipment. The electronic nose, on the other hand, can provide faster results and is particularly useful for routine operation. Several examples are available in the literatures, demonstrating the success of using polymeric array of sensors for the detection of organic vapour.

Chen *et al.* (2005) studied the gas sensor based on conductive composite materials comprised of carbon black and waterborne polyurethane. They found that the composites responded to a series of vapours of polar and non-polar solvents. Moreover, it showed the property to distinguish and quantify the organic vapours.

Wang *et al.* (2007) prepared the composites of carbon black homo- and copolymers of styrene and 4-vinylpyridine, synthesized by a nitroxide-mediated “living” free radical method, for the detection of methanol vapour.

MATERIALS AND METHOD

Materials

PVA with molecular weight of 22,000 (shown on label) was purchased from MP Biomedicals, LLC (France). Benzoyl chloride and *p*-Toluoly chloride were purchased from Panreac Sintesis (Spain) and Fluka (Japan), respectively. Triethylamine was obtained from Fluka (Belgium). Conductive grade carbon black (CB) was obtained from Degussa Company. All solvents (dichloromethane (CH_2Cl_2), hexane, toluene, diethyl ether, ethyl acetate, tetrahydrofuran (THF), dioxane, acetonitrile, methanol, ethanol, iso-propanol, and dimethyl sulfoxide (DMSO)) were obtained from LAB-SCAN Analytical Sciences (Thailand).

Instruments

FTIR spectra were measured with a fourier transform infrared spectrophotometer: Shimadzu partige 21 with 45 scans at a resolution 16 cm^{-1}. ^1H-NMR spectra were recorded using INNOVA VARION NMR spectrometer with working frequency 400 MHz. Elemental analysis was performed with a LECO CHNS-932. The molecular weight of PVA dissolved in water was determined by a Waters 600E GPC equipped with ultrahydrogel linear 1 column (eluent: 0.1 M $NaNO_3$, flow rate: 0.6 mL/min, at 30^oC) while that of esterified PVA dissolved in THF was investigated by a Breeze GPC (model: Isocratic HPLC Pump 1515) equipped with Styragel HR 3, 4, and 6 THF column (eluent: THF, flow rate: 1.0 mL/min, at 40^oC).

The thickness of film was investigated by surface profiler, Dektak^{3}ST. The resistance of chemical sensors was measured by a digital multimeter (Keithley 2700). The surface morphology of composite film was observed by optical microscope.

Methods

1. Characterization of poly(vinyl alcohol)

Before modification, the poly(vinyl alcohol) was dissolved in various organic solvents to ascertain the good solvent. The solubility test was carried out by weighing 0.1 g of the polymer and then dissolving in 1 mL of each organic solvent at room temperature. The structure of PVA was studied by FTIR, ^{1}H-NMR, elemental analysis, and GPC.

2. Synthesis and characterization of modified polymers

2.1. Poly(vinyl alcohol) modified with benzoyl chloride

PVA (5.50 g, 0.25 mmol of vinyl alcohol repeat units), triethylamine (17.55 mL, 125 mmol) and 1,4-dioxane (100 mL) were mixed in a round-bottom flask. The reaction mixture was refluxed with continuously stirring for 1 h (Figure 2). Benzoyl chloride (14.52 mL, 125 mmol) was, then, added dropwise into the solution. To complete the reaction, the solution was further refluxed for 3 h until the solution changed colour. Then, the mixture product was filtered to separate off solid triethylammonium chloride. The filtrate was removed the solvent by a vacuum evaporator to obtain the viscous product which was dissolved in CH_2Cl_2 and extracted several times with distilled water. The purified product solution was dried over anhydrous sodium sulphate, removed the solvent and solidified in diethyl ether to obtain the esterified PVA. The product obtained was characterized by FTIR, ^{1}H-NMR, elemental analysis, and GPC. Moreover, the solubility of the product in various organic solvents was also determined.

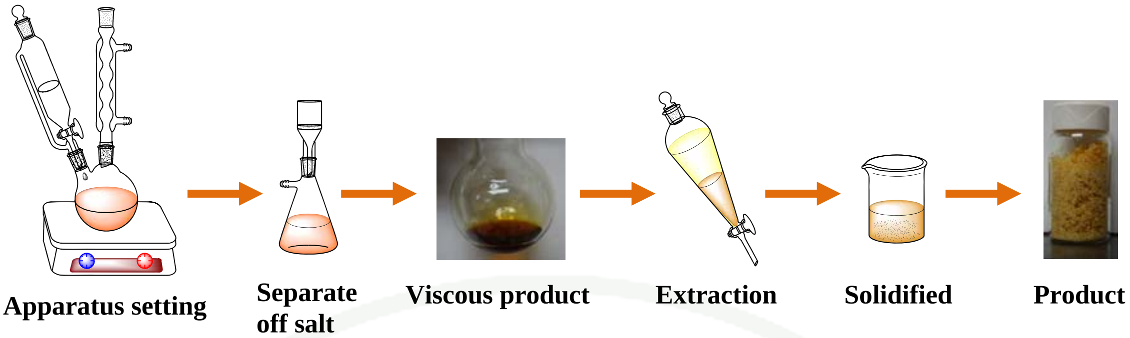


Figure 2 The procedure of polymer synthesis.

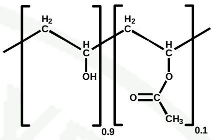
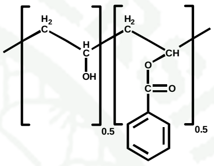
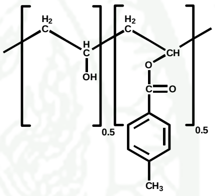
2.2. Poly(vinyl alcohol) modified with *p*-toluoyl chloride

Similarly, poly(vinyl alcohol) modified with *p*-toluoyl chloride was synthesized as the same method for synthesizing poly(vinyl alcohol) modified with benzoyl chloride. The starting material as *p*-toluoyl chloride (16.53 mL, 125 mmol) was used instead of benzoyl chloride. The purified product was identified by FTIR, ^{1}H-NMR, elemental analysis, and GPC. The solubility of the obtained product in various organic solvents was investigated.

3. Fabrication of sensors

The series of composite mixtures were prepared in DMSO by adding various amounts of carbon black (10-100 %w/w) into a polymer solutions in which its concentration was fixed at 50 mg/mL. Composite mixtures were coated on the interdigited electrodes (IDE), made by thermal evaporation of chromium (Cr, 20 nm) and gold (Au, 200 nm) on a glass slide, by spin coating technique at spin speed 2000 rpm for 5 min. The thickness of composite films was investigated by surface profiler, Dektak^{3}ST. The surface morphology of composite films was also determined by optical microscope. The resistance of chemical sensors was measured by a digital multimeter in order to determine the percolation threshold of the composites. The polymers and their structures used as coating materials were shown in Table 1.

Table 1 Coating materials and their chemical structures fabricated as sensor materials**.**

Coating material	Chemical structure
PVA	
PVA modified with benzoyl chloride	
PVA modified with *p*-toluoyl chloride	

4. Sensing measurement of sensors

The sensing measurements of polymer sensor arrays in various gas media were performed with the experimental setup shown in Figure 3. All experiments were measured at room temperatures of 25°C and atmospheric pressure of 1 atm. The measurements were performed in the unidirectional gas-glow system with the only contact with surrounding air at the exhaust outlet so that the environmental humidity does not affect the measurement results. A sensing measurement started by allowing pure N_2 gas into the sensor chamber at 600 mL/min for 60 sec to run the background. N_2 gas carried a saturated vapour of organic solvent in the bottle (100 mL) was loaded with 60 mL solvent to the sensor chamber for 15 s (sniffing time). The changes of film resistivity upon the influence of saturated vapours of the volatile organic compounds (hexane, toluene, iso-propanol, THF, ethyl acetate, 1,4-dioxane, methanol, ethanol, acetonitrile, DMSO, and water) were recorded by a digital multimeter (Keithley 2700). After each measurement, the sensors were cleaned by continuous blowing with pure N_2 gas for 600 s (recovery time) at the flow rate of 600 mL/min. The total steps were reproduced for 5 times. The total electrical data was collected and calculated by the computer.

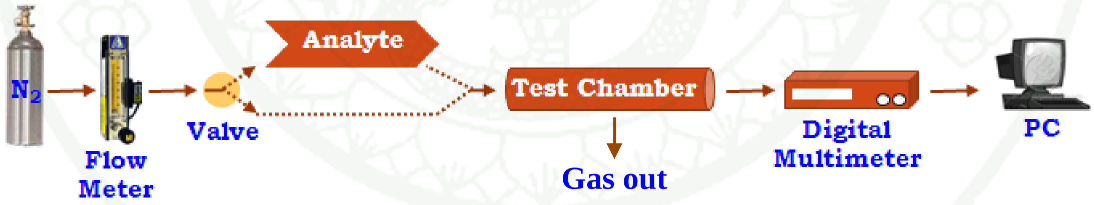


Figure 3 Schematic view of the experimental setup.

RESULTS AND DISCUSSION

1. Characterization of poly(vinyl alcohol)

FTIR spectrometer was used to determine the functional groups of poly(vinyl alcohol). From Figure 4, the appearance of absorption peak between 3700 and 3300 cm^{-1} indicates the presence of strong intermolecular and intramolecular hydrogen bonding among hydroxyl groups. The C–H stretching and C-O vibration were observed at about 2947 and 1450 cm^{-1}, respectively. In addition, the absorption peak of 1149 cm^{-1} was referred to the crystalline poly(vinyl alcohol) (Sundararajan, 1999).

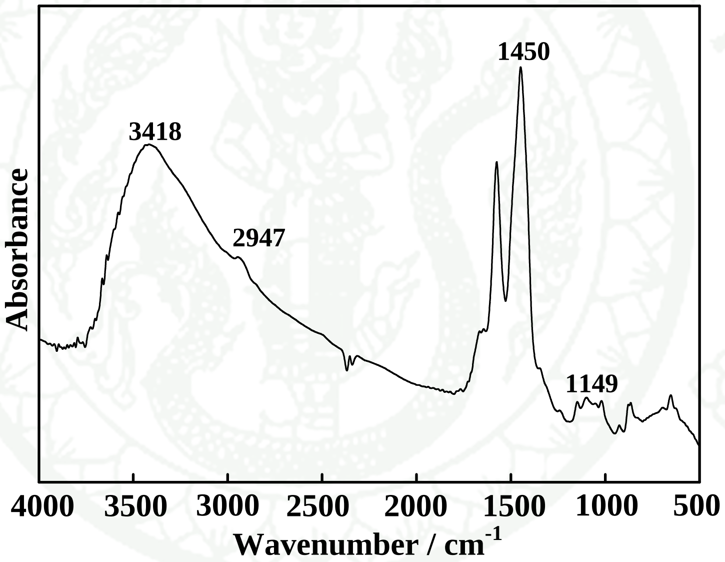


Figure 4 FTIR spectrum of poly(vinyl alcohol).

^{1}H-NMR spectrometer was used to distinguish the protons on the poly(vinyl alcohol) chain and to determine the amount of acetyl group remained (hydrolysis percentage) by calculation of integral area of each proton type. The ^{1}H-NMR spectrum for the poly(vinyl alcohol) was shown in Figure 5 and the ^{1}H-NMR results were shown as follows.

PVA: ^{1}H NMR (DMSO-d6, δ in ppm): 1.30-1.69 (2H, $-CH(OH)-C\underline{H}_2-$), 1.70-1.90 (2H, $-CH(CO_2CH_3)-C\underline{H}_2-$), 1.85-2.05 (3H, $-CH(CO_2C\underline{H}_3)-$), 3.25-3.45 (1H,-$CH(OH)-C\underline{H}(OH)-$), 3.50-3.70 (2H, $-C\underline{H}_2(OH)$), 3.70-4.00 (1H, $-CH_2-C\underline{H}(OH)-$), 4.15-5.00 (1H, $-O\underline{H}$), 5.10-5.20 (1H, $-C\underline{H}(CO_2CH_3)-$).

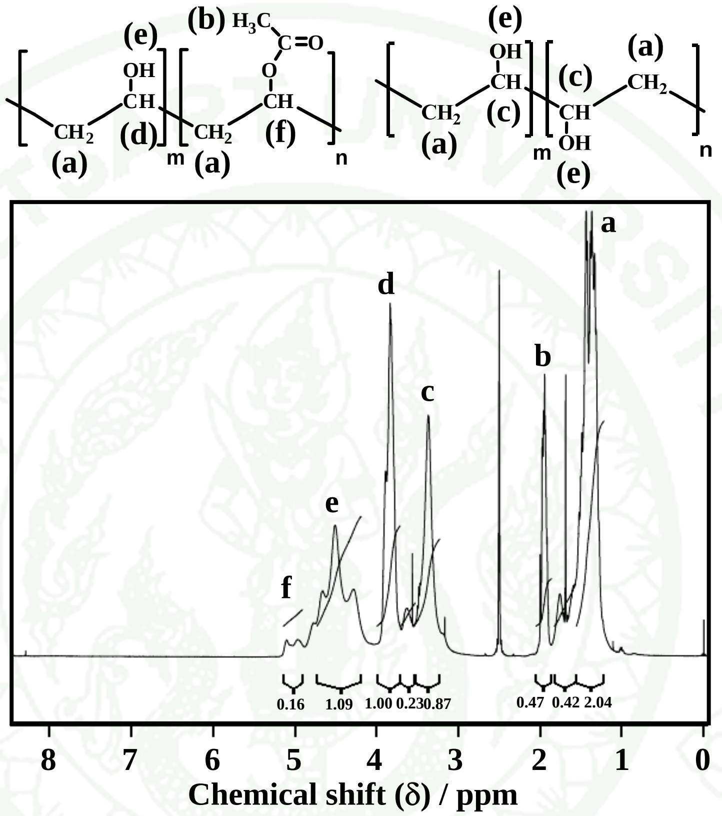


Figure 5 ^{1}H-NMR spectrum of poly(vinyl alcohol).

The hydrolysis percentage, determined by comparing the integral area of total methylene (CH_2) and methane (CH) protons of poly(vinyl alcohol) with the integral area of methyl protons of acetyl groups, was calculated as follows.

Total integral area of methylene protons	: 2.04+0.42+0.23	= 2.69
Total integral area of methine protons	:0.87+1.00+0.16	= 2.03
So, total integral areas of protons on main chain	:	= 4.72
The integral area of methyl protons of acetyl groups	:	= 0.47
Hence, %hydrolysis of poly(vinyl alcohol)	:(0.47x100%)/4.72	= 9.96 %

From the calculation, it was found the hydrolysis percentage is around 10 %.

To confirm hydrolysis percentage calculated from ^{1}H-NMR technique, the elemental analysis (CHN analysis) technique was carried out to determine the amount of the elements in PVA.

Table 2 Elemental analysis results of poly(vinyl alcohol).

No.	Sample weight (mg)	%C	%H	%O
1	2.068	51.97	8.75	39.28
2	2.063	51.89	8.56	39.55
3	2.102	51.89	8.51	39.60
Average		51.92	8.61	39.48
Theory (90% Hydrolysis of PVA)		54.77	8.71	36.51

The elemental analysis results were shown in Table 2 while the theoretical calculation of the CHO percentage was shown as follows.

Calculation of the weight percent of each element in the poly(vinyl alcohol)

The poly(vinyl alcohol) assumed as 90% hydrolysis has the formula as -$(C_2H_4O)_{0.9}(C_4H_6O_2)_{0.1}$- while the molecular weight of the average repeating unit was 48.2.

$$\%C = \frac{[0.9\text{x}2\,(\text{mole C}) + 0.1\text{x}4\,(\text{mole C})]\ \text{x}\ 12.01\,(\text{g/mole C})}{48.2\,(\text{g/mole})}\ \text{x}\ 100\%$$

$$= 54.77\ \%$$

$$\%H = \frac{[0.9\text{x}4\,(\text{mole H}) + 0.1\text{x}6\,(\text{mole H})]\ \text{x}\ 1.01\,(\text{g/mole H})}{48.2\,(\text{g/mole})}\ \text{x}\ 100\%$$

$$= 8.71\ \%$$

$$\%O = \frac{[0.9\text{x}1\,(\text{mole O}) + 0.1\text{x}2\,(\text{mole O})]\ \text{x}\ 16.00\,(\text{g/mole O})}{48.2\,(\text{g/mole})}\ \text{x}\ 100\%$$

$$= 36.51\ \%$$

From elemental analysis results, it was found that the CHO percentage obtained was not significantly different from the theoretical calculation.

The molecular weight of poly(vinyl alcohol) was determined by GPC technique. Water was used as solvent while pollulans (M_w: 5900-788,000) was used as standard agent. The number average molecular weight ($\overline{M_n}$) and the weight average molecular weight ($\overline{M_w}$) were found to be around 8,200 Da and 33,000 Da, respectively. The polydispersity index (PDI) of poly(vinyl alcohol) was, therefore, 4.01. It implies that the molecular weight distribution of poly(vinyl alcohol) was polydisperse distribution. By using the result of $\overline{M_w}$, the number of repeating unit of poly(vinyl alcohol) were calculated as follows.

Calculation of repeating unit of poly(vinyl alcohol)

Based on ^{1}H-NMR result, it was found that the hydrolysis percentage of poly(vinyl alcohol) is around 10%. The percentage ratio between the vinyl alcohol repeating unit and the vinyl acetate repeating unit is 9 to 1. The molecular weight of the vinyl alcohol repeating unit and that of the vinyl acetate repeating unit were 44.05 and 86.09, respectively. The weight average molecular weight ($\overline{M_w}$) of a poly(vinyl alcohol) from GPC was 33,000, the number of repeating units of a poly(vinyl alcohol) (R) were calculated as follows.

$$M_w \text{ of PVA} = R \times [(0.9 \times M_w \text{ of vinyl alcohol repeating unit}) + (0.1 \times M_w \text{ of vinyl acetate repeating unit})]$$

$$33{,}000 = R \times [(0.9 \times 44.05) + (0.1 \times 86.09)]$$

$$R = 684 \text{ units}$$

Hence, the number of repeating units of poly(vinyl alcohol) were 684 units.

The results of the solubility test for poly(vinyl alcohol) were shown in Table 3. It was found that the poly(vinyl alcohol) could be only dissolved in the polar solvents having high solubility parameter value, such as, DMSO, alcohol, and water (most) due to the plenty of hydroxyl groups in the structure of poly(vinyl alcohol).

Table 3 Solubility of the poly(vinyl alcohol) in various organic solvents**.**

No.	Solvent (1 mL)	Solubility parameters $(cal/cm^3)^{1/2}$	Solubility (0.1 g/mL, 25°C)
1	Hexane	7.3	insoluble
2	Diethyl ether	7.4	insoluble
3	iso-Propanol	8.8	insoluble
4	Toluene	8.9	insoluble
5	Ethyl acetate	9.1	insoluble
6	THF	9.1	insoluble
7	Dioxane	10.0	insoluble
8	Acetonitrile	11.9	insoluble
9	DMSO	12.0	soluble
10	Ethanol	12.9	soluble
11	Methanol	14.5	soluble
12	Water	23.9	soluble

Source: Eds. Brandrup *et.al.*, 1999

2. Synthesis and characterization of modified poly(vinyl alcohol)

2.1. Characterization of poly(vinyl alcohol) modified with benzoyl chloride

After PVA reacted with benzoyl chloride, the brown product obtained was studied by FTIR technique. The spectra of poly(vinyl alcohol) and poly(vinyl alcohol) modified with benzoyl chloride were shown in Figure 6. From FTIR spectrum of poly(vinyl alcohol) modified with benzoyl chloride, the C=O vibration of ester at 1712 cm^{-1} was found indicating that the hydroxyl group of poly(vinyl alcohol) reacted with acid chloride to produce the esterified poly(vinyl alcohol) as a product. The C–H stretching of aromatic and aliphatic vibrations was observed at 3062 and 2924 cm^{-1}, respectively. However, a broad peak between 3300 and 3700 cm^{-1} indicating the presence of strong hydrogen bonding of hydroxyl groups was found. As comparing with spectrum of PVA, it illustrates that all of the hydroxyl groups of PVA did not completely react with benzoyl chloride.

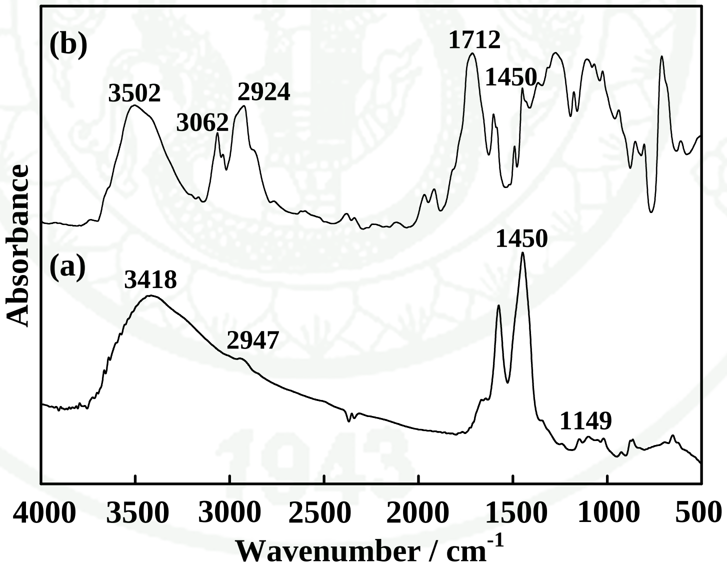


Figure 6 FTIR spectra of poly(vinyl alcohol) (a) before and (b) after modifying with benzoyl chloride.

Only from FTIR result (Figure 6), the amount of ester groups on PVA could not be quantified. ^{1}H-NMR technique was, then, carried out to calculate the total amount of acid chloride reacting with poly(vinyl alcohol) or the conversion of esterified poly(vinyl alcohol) by measuring the increment of the integral area of the chemical shift, 7.00-7.95 ppm (aromatic protons of benzoyl group) and comparing with the integral area of methylene protons, 1.30-2.20 ppm (Figure 7). It was found that although the excess amount of benzoyl chloride was employed and the reaction conditions were varied, the conversion of esterified poly(vinyl alcohol) was about 50%. The broad peak referred to hydroxyl groups in FTIR spectrum of esterified poly(vinyl alcohol) was, therefore, found. It might be due to the esterification was limited by the configuration of PVA structure and steric effect from the benzoyl group to react with hydroxyl groups of PVA. Because of benzoyl group stable than acetyl group, acetyl group reacted transesterification with benzoyl chloride. The ^{1}H-NMR results of esterified poly(vinyl alcohol) were shown as follows.

Poly(vinyl alcohol) modified with benzoyl chloride: ^{1}H NMR (DMSO-d_6, δ in ppm): 1.30-2.20 (2H, $-C\underline{H}_2-$), 3.30-3.35 (1H, $-CH-C\underline{H}(OH)-$), 3.45-3.75 (1H, $-CH_2-C\underline{H}(OH)-$), 4.25-4.85 (1H, $-O\underline{H}$), 5.00-5.40 (1H, $-C\underline{H}(CO_2C_6H_5)-$), 7.00-7.95 (5H, $-C_6\underline{H}_5$).

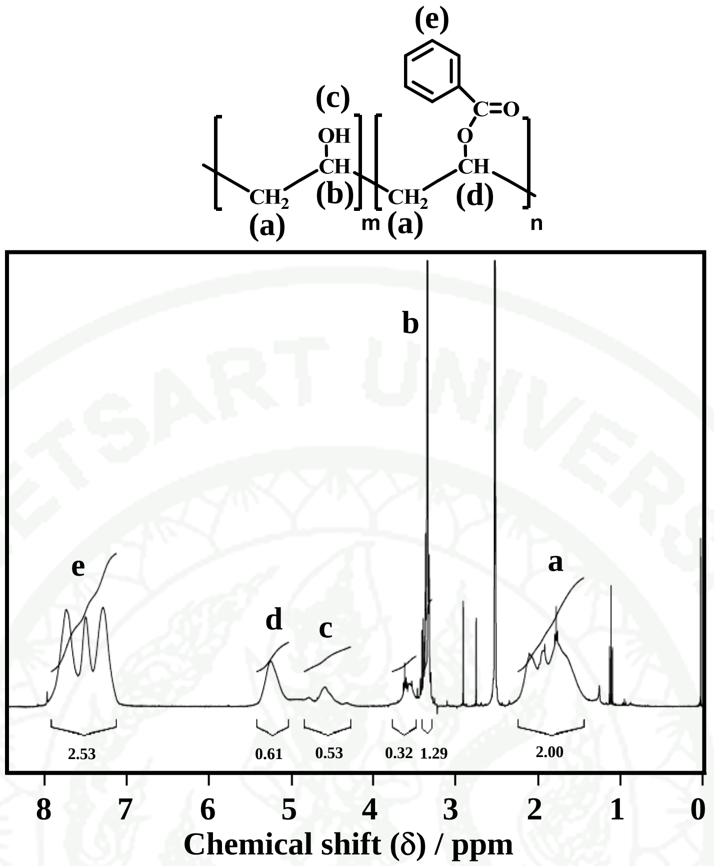


Figure 7 ^{1}H-NMR spectrum of poly(vinyl alcohol) modified with benzoyl chloride.

Similarly, the esterified percentage calculated from ^{1}H-NMR technique was confirmed by elemental analysis as shown in Table 4.

Table 4 Elemental analysis results of poly(vinyl alcohol) modified with benzoyl chloride.

No.	Sample weight (mg)	%C	%H	%O
1	2.008	68.43	6.09	25.48
2	2.098	67.98	5.98	26.04
3	2.089	68.29	6.05	25.66
Average		68.23	6.04	25.72
Theory (50% modified PVA)		68.81	6.31	25.00

The elemental analysis results of modified poly(vinyl alcohol) were shown in Table 4 while the theoretical calculation of the CHO percentage was shown as follows.

Calculation of the weight percent of each element in the poly(vinyl alcohol) modified with benzoyl chloride

The formula structure of the 50% modified poly(vinyl alcohol) is $-(C_2H_4O)_{0.5}(C_9H_8O_2)_{0.5}-$ while the molecular weight of the average repeating unit is 96. Therefore,

$$\%C = \frac{[0.5\text{x}2\text{ (mole C)} + 0.5\text{x}9\text{ (mole C)}]\text{ x }12.01\text{ (g/mole C)}}{96\text{ (g/mole)}}\text{ x }100\%$$

$$= 68.81\ \%$$

$$\%H = \frac{[0.5\text{x}4\text{ (mole H)} + 0.5\text{x}8\text{ (mole H)}]\text{ x }1.01\text{ (g/mole H)}}{96\text{ (g/mole)}}\text{ x }100\%$$

$$= 6.31\ \%$$

$$\%O = \frac{[0.5\text{x}1\text{ (mole O)} + 0.5\text{x}2\text{ (mole O)}]\text{ x }16.00\text{ (g/mole O)}}{96\text{ (g/mole)}}\text{ x }100\%$$

$$= 25.00\ \%$$

The results showed that the theoretical calculation percentage of modified poly(vinyl alcohol) and CHO percentage obtained were not distinct. It can be concluded that the poly(vinyl alcohol) actually reacted with benzoyl chloride only 50% of repeating units of poly(vinyl alcohol).

The molecular weight of poly(vinyl alcohol) modified with benzoyl chloride was characterized by GPC. Tetrahydrofuran and polystyrene were employed as a solvent and standard reagent, respectively. It was found that the number average molecular weight ($\overline{M_n}$) was about 36,000 Da while the weight average molecular weight ($\overline{M_w}$) was about 81,000 Da. The polydispersity index (PDI) of modified poly(vinyl alcohol) was 2.27.

Based on the calculated repeating unit of poly(vinyl alcohol), it was found to be about 684 units. The molecular weight of the vinyl alcohol repeating unit and that of the vinyl benzoate repeating unit were 44 and 148, respectively. The $\overline{M_w}$ of the 50% esterified poly(vinyl alcohol) by benzoyl chloride was, therefore, around 65,664 Da ($\overline{M_w}$ = (0.5x684x148) + (0.5x684x44) = 65,664). It illustrated that the calculated molecular weight was different from the molecular characterized by GPC. It might be the fact that the unmodified and the modified poly(vinyl alcohol)s were dissolved in different solvents before measuring be GPC since the polarity of the modified poly(vinyl alcohol) was changed from the modified poly(vinyl alcohol). By using different polarity solvents, it might affect to the hydrodynamic volumes of the unmodified and modified poly(vinyl alcohol)s resulting in dissimilar size and shape of polymers in the solution.

The solubility of the modified poly(vinyl alcohol) was investigated and the results were shown in Table 5. It was found that the polarity of the modified poly(vinyl alcohol) was decreased as comparing with the unmodified poly(vinyl alcohol) (Table 3). The modified poly(vinyl alcohol) was soluble in solvents having solubility parameters ranging from 9 to 12, such as, etheyl acetate, THF, dioxane, acetonitrile, and DMSO.

Table 5 Solubility of the poly(vinyl alcohol) modified with benzoyl chloride in various organic solvents**.**

No.	Solvent (1 mL)	Polarity Index	Solubility (0.1 g/mL, 25°C)
1	Hexane	0	insoluble
2	Diethyl ether	2.8	insoluble
3	iso-Propanol	3.9	insoluble
4	Toluene	2.4	insoluble
5	Ethyl acetate	4.4	soluble
6	THF	4.0	soluble
7	Dioxane	4.8	soluble
8	Acetonitrile	5.8	soluble
9	DMSO	7.2	soluble
10	Ethanol	5.2	insoluble
11	Methanol	5.1	insoluble
12	Water	9.0	insoluble

Source: J.A. Byers, 2003

2.2. Characterization of poly(vinyl alcohol) modified with *p*-Toluoyl chloride

The brown product obtained was studied by FTIR technique. The FTIR spectrum of poly(vinyl alcohol) modified with *p*-toluoyl chloride (Figure 8) shows C-H stretching of aromatic and aliphatic vibration at 3032 and 2924 cm^{-1}, respectively. The C=O vibration at 1712 cm^{-1} of ester assures that the poly(vinyl alcohol) reacted with *p*-toluoyl chloride. However, a broad peak of hydroxyl group at 3495 cm^{-1} still appeared implying the uncompleted reaction occurred on the hydroxyl groups of poly(vinyl alcohol) as similar as the case of poly(vinyl alcohol) modified with benzoyl chloride.

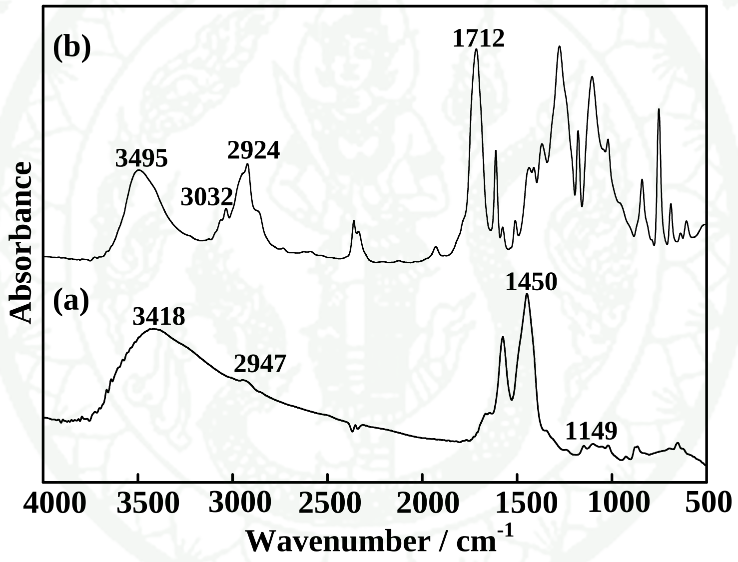


Figure 8 FTIR spectra of poly(vinyl alcohol) (a) before and (b) after modifying with *p*-toluoyl chloride.

^{1}H-NMR spectrum of poly(vinyl alcohol) modified with benzoyl chloride was shown in Figure 9 and results were presented as follows.

Poly(vinyl alcohol) modified with *p*-toluoyl chloride: ^{1}H NMR (DMSO-d6, δ in ppm): 0.96-2.20 (2H, $-C\underline{H}_2-$), 2.15-2.43 (3H, $C\underline{H}_3$), 3.26-3.63 (1H, $-CH-C\underline{H}(OH)-$), 4.19-4.83 (1H, $-CH_2-C\underline{H}(OH)-$), 4.86-5.49 (1H, $-O\underline{H}$), 6.83-7.86 (4H, $-C_6\underline{H}_4CH_3$).

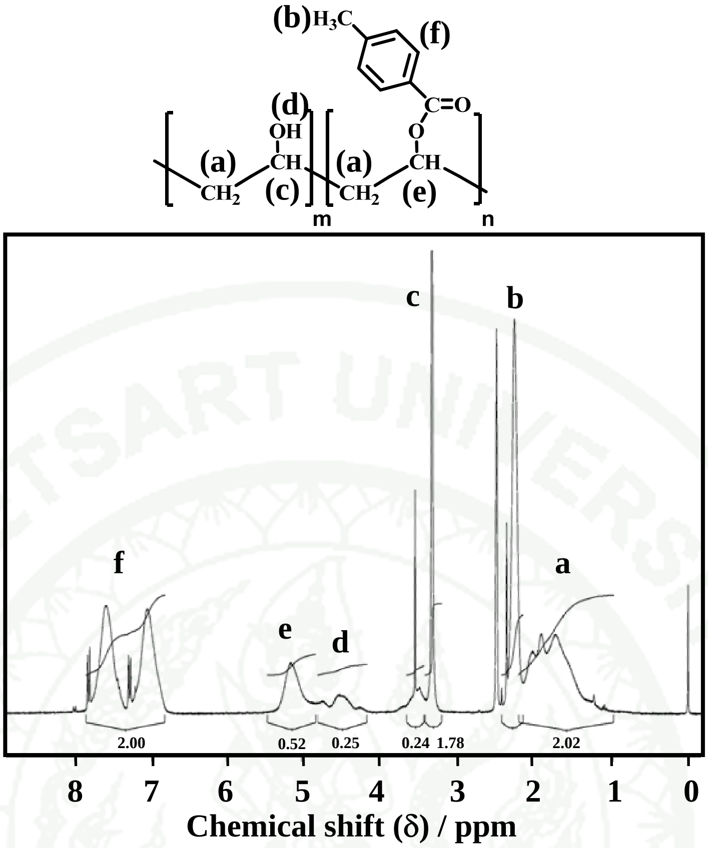


Figure 9 ^{1}H-NMR spectrum of poly(vinyl alcohol) modified with *p*-toluoyl chloride.

The conversion of esterified poly(vinyl alcohol), quantitatively analyzed by ^{1}H-NMR, was calculated by comparing the integrated intensities of the signals appearing in the interval 6.83-7.86 ppm (corresponding to the aromatic protons) with the peak at 0.96-2.20 ppm (ascribing to the methylene protons in the main chain). It was found that the conversion of poly(vinyl alcohol) modified with *p*-toluoyl chloride was around 50% as well as the conversion of poly(vinyl alcohol) modified with benzoyl chloride.

The hydrolysis percentage calculated from ^{1}H-NMR technique was confirmed by Elemental analysis and the results were presented in Table 6.

Table 6 Elemental analysis results of poly(vinyl alcohol) modified with *p*-toluoyl chloride.

No.	Sample weight (mg)	%C	%H	%O
1	2.048	70.53	6.81	22.66
2	2.020	70.48	6.78	22.74
3	2.037	70.55	6.78	22.67
Average		70.52	6.79	22.69
Theory (50% modified PVA)		69.96	6.86	23.30

Calculation of the weight percent of each element in the poly(vinyl alcohol) modified with *p*-toluoyl chloride

The formula structure of the 50% modified poly(vinyl alcohol) is presented as $-(C_2H_4O)_{0.5}(C_{10}H_{10}O_2)_{0.5}-$ while the molecular weight of the repeating unit is 103.

$$\%C = \frac{[0.5x2\,(\text{mole C}) + 0.5x10\,(\text{mole C})]\ x\ 12.01\,(\text{g/mole C})}{103\,(\text{g/mole})}\ x\ 100\%$$

$$= 69.96\ \%$$

$$\%H = \frac{[0.5x4\,(\text{mole H}) + 0.5x10\,(\text{mole H})]\ x\ 1.01\,(\text{g/mole H})}{103\,(\text{g/mole})}\ x\ 100\%$$

$$= 6.86\ \%$$

$$\%O = \frac{[0.5x1\,(\text{mole O}) + 0.5x2\,(\text{mole O})]\ x\ 16.00\,(\text{g/mole O})}{103\,(\text{g/mole})}\ x\ 100\%$$

$$= 23.30\ \%$$

The results from Table 6 showed that the theoretical calculation percentage of modified poly(vinyl alcohol) and CHO percentage obtained were not distinct. It can be concluded that the poly(vinyl alcohol) actually reacted with *p*-toluoyl chloride only 50% of repeating units of poly(vinyl alcohol).

By using GPC, the molecular weight of poly(vinyl alcohol) modified with *p*-toluoyl chloride was investigated. Tetrahydrofuran was used as a solvent and polystyrene was used as a standard reagent. The number average molecular weight ($\overline{M_n}$) and the weight average molecular weight ($\overline{M_w}$) were found to be 31,166 Da and 72,762 Da, respectively. The polydispersity index (PDI) of poly(vinyl alcohol) modified with *p*-toluoyl chloride was 2.33.

Since the repeating unit of poly(vinyl alcohol) from calculation was about 684 units while the molecular weights of the vinyl alcohol repeating unit and the vinyl p-methylbenzoate repeating unit were 44 and 162, respectively. The $\overline{M_w}$ of the 50% esterified poly(vinyl alcohol) by *p*-toluoyl chloride was, thus, around 70,452 Da ($\overline{M_w}$ = (0.5x684x162) + (0.5x684x44) = 70,452). The results showed that the calculated molecular weight was slightly different from the molecular characterized by GPC due to the polarity and hydrodynamic volume of modified poly(vinyl alcohol).

The solubility of the poly(vinyl alcohol) modified with *p*-toluoyl chloride was studied and the results were shown in Table 7. It was found that the poly(vinyl alcohol) modified with *p*-toluoyl chloride was soluble in solvents having solubility parameters ranging between 9 and 12, such as, etheyl acetate, THF, dioxane, acetonitrile, and DMSO. The results exhibited that the polarity of the modified poly(vinyl alcohol) with *p*-toluoyl chloride decreased as comparing with the unmodified poly(vinyl alcohol) (Table 3).

Table 7 Solubility of the poly(vinyl alcohol) modified with *p*-toluoyl chloride in various organic solvents**.**

No.	Solvent (1 mL)	Polarity Index	Solubility (0.1 g/mL, 25^{o}C)
1	Hexane	0	insoluble
2	Diethyl ether	2.8	insoluble
3	iso-Propanol	3.9	insoluble
4	Toluene	2.4	insoluble
5	Ethyl acetate	4.4	soluble
6	THF	4.0	soluble
7	Dioxane	4.8	soluble
8	Acetonitrile	5.8	soluble
9	DMSO	7.2	soluble
10	Ethanol	5.2	insoluble
11	Methanol	5.1	insoluble
12	Water	9.0	insoluble

Source: J.A. Byers, 2003

3. Fabrication of sensors

3.1. The thickness of polymer films

In this present work, the concentration of polymers for film preparation was fixed at 50 mg/cm^3. The thicknesses of poly(vinyl alcohol), poly(vinyl alcohol) modified with benzoyl chloride, and poly(vinyl alcohol) modified with *p*-toluoyl chloride film were found to be 252, 380 and 405 nm, respectively. All of the films were measured in the saturated condition of each solvent; therefore, the effect of film thickness might be eliminated.

3.2. Percolation threshold of unmodified and esterified poly(vinyl alcohol) composites

The response mechanism of the carbon black/polymer composite sensor can be explained by percolation theory describing the relationship between the conductivity or resistivity of the composite and carbon black content. The low conductivity of the composites will be generated when the concentration of carbon black in composite is too low to form the conductive network. By increasing the concentration of carbon black, the conductivity of the composites was gradually increases until the carbon network forms. This is called as the percolation threshold resulting in the conductivity of the composite suddenly increases. After percolation threshold point, the conductance of composite obscurely changes.

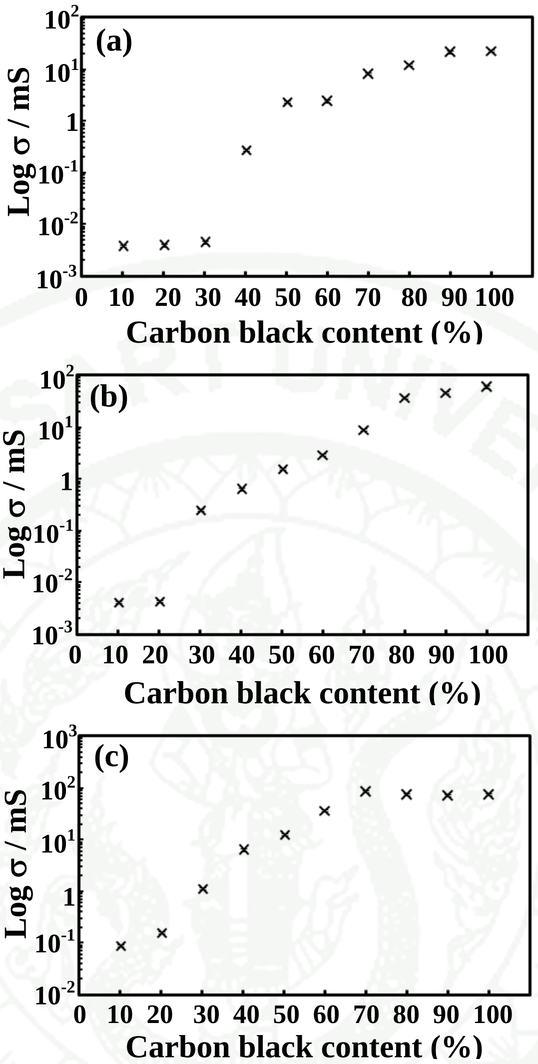


Figure 10 The percolation threshold of composite films of (a) CB/PVA, (b) CB/PVA modified with benzoyl chloride, and (c) CB/PVA modified with *p*-toluoyl chloride.

Accordingly, the percolation threshold of the each composite, plotted between conductance and carbon black content, was shown in Figure 10. The percolation thresholds of poly(vinyl alcohol), poly(vinyl alcohol) modified with benzoyl chloride, and poly(vinyl alcohol) modified with *p*-toluoyl chloride were found to be 40, 30, and 30 %CB, respectively. From the section 3.1, it was found that the thickness of the CB/PVA composite film was thinner than that of the CB/ PVA modified with acid chloride composites films, the percolation threshold of CB/PVA composite was, then, higher than the composites of CB/ PVA modified with acid chloride.

3.3. The surface morphology of composite films

From the section 3.2, the percolation thresholds of poly(vinyl alcohol), poly(vinyl alcohol) modified with benzoyl chloride, and poly(vinyl alcohol) modified with *p*-toluoyl chloride were found to be 40, 30, and 30%CB. To confirm the existence of conductive network in composites, the surface morphology of composite films was studied as shown in Figures 11-13. It was found that the composite films with the carbon black percentage lower than percolation threshold did not show the conductive networks as shown in Figures 11(a), 12(a) and 13(a) for poly(vinyl alcohol), poly(vinyl alcohol) modified with benzoyl chloride, and poly(vinyl alcohol) modified with *p*-toluoyl chloride, respectively. In contrast, Figures 11(b), 12(b) and 13(b) showed the existence of conductive network in composite film with carbon black percentage as the percolation thresholds. Therefore, the conductance instantaneously increased for the composite films at the percolation thresholds as shown in Figure 10.

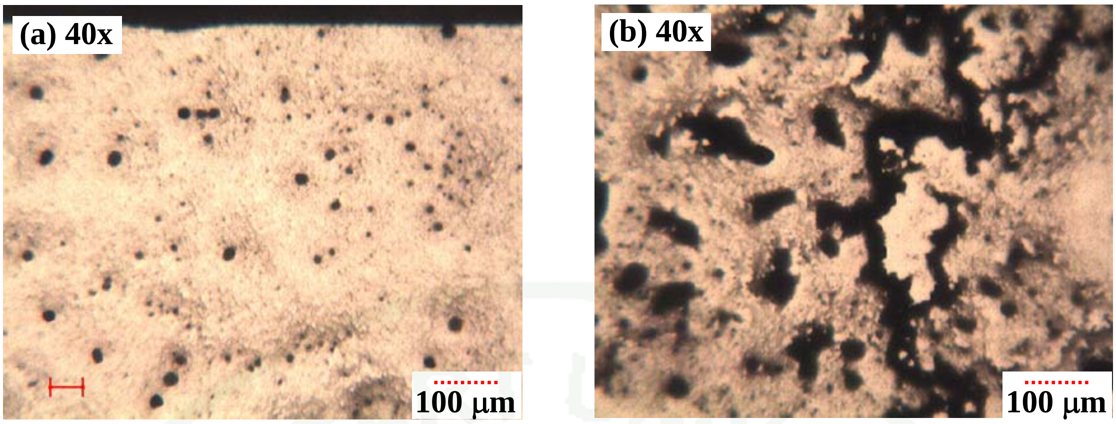


Figure 11 The surface morphology of CB/PVA composite film of (a) 30% CB and (b) 40% CB.

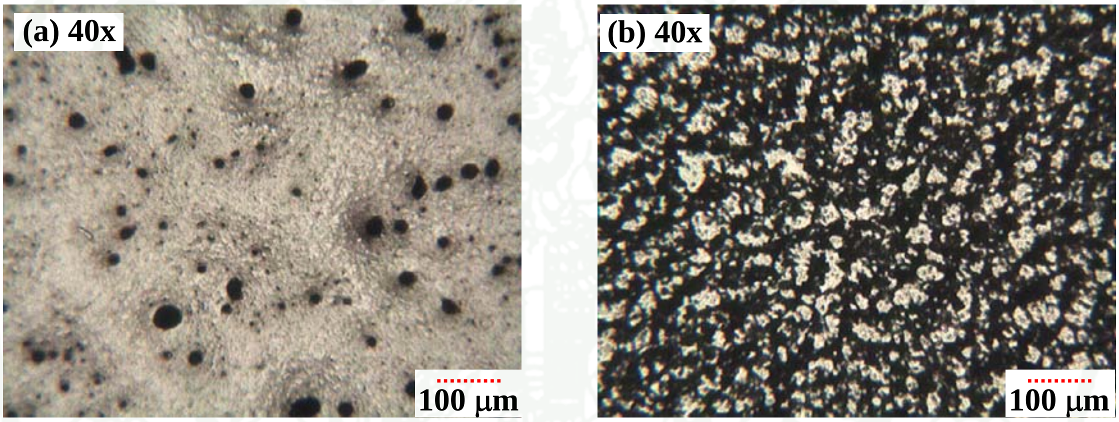


Figure 12 The surface morphology of CB/PVA modified with benzoyl chloride composite film of (a) 20% CB and (b) 30% CB.

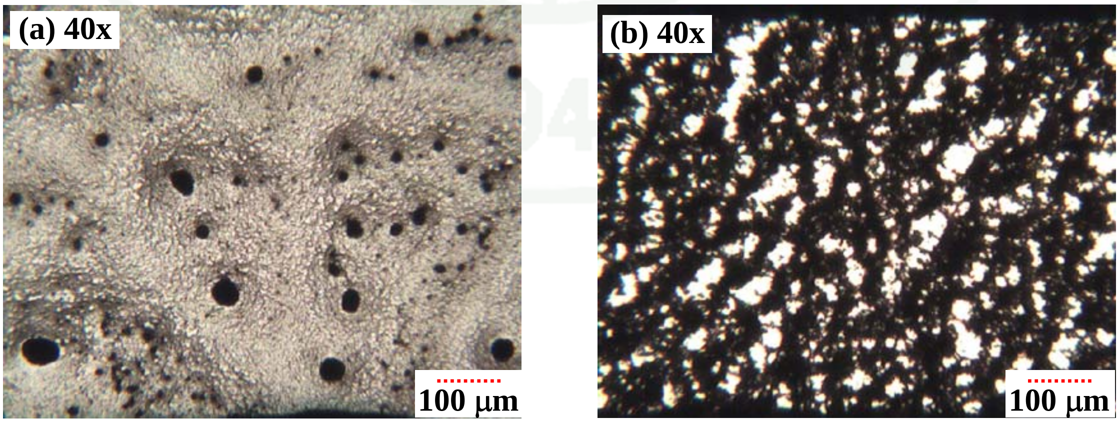


Figure 13 The surface morphology of CB/PVA modified with *p*-toluoyl chloride composite film of (a) 20% CB and (b) 30% CB.

4. Sensing measurement of sensors

4.1. Responsibility of sensors

According to the rule of “like dissolves like”, the swelling of polymers is generated due to the interaction between polymer and solvent. The response of the polymer composite film was induced when the polymer film exposed to the vapour of each solvent was swollen. In addition, the degree of swelling upon the type of solvents is proportional to the change in resistance of the polymer film. It was due to the number of conductive pathways in the polymer film decrease with increasing in the degree of swelling. The electrical resistivity of each sensor is, therefore, measured and the response of sensor in the array is expressed as dR/R_o or $(R_{max}-R_o)/R_o$. The R_{max} denotes the maximum resistance of a composite in certain chemical vapour while the R_o is the initial resistance of a composite.

The 40% CB/PVA composite clearly responded to methanol and water while the others solvent were slightly responded to the composite (Figure 14(a)) . In the case of the modified poly(vinyl alcohol) composite films, they widely responded to various organic vapours (Figure 14(b)). In addition, the 30% CB/PVA modified with *p*-toluoyl chloride showed the high sensitivity to ethyl acetate (Figure 14(c)).

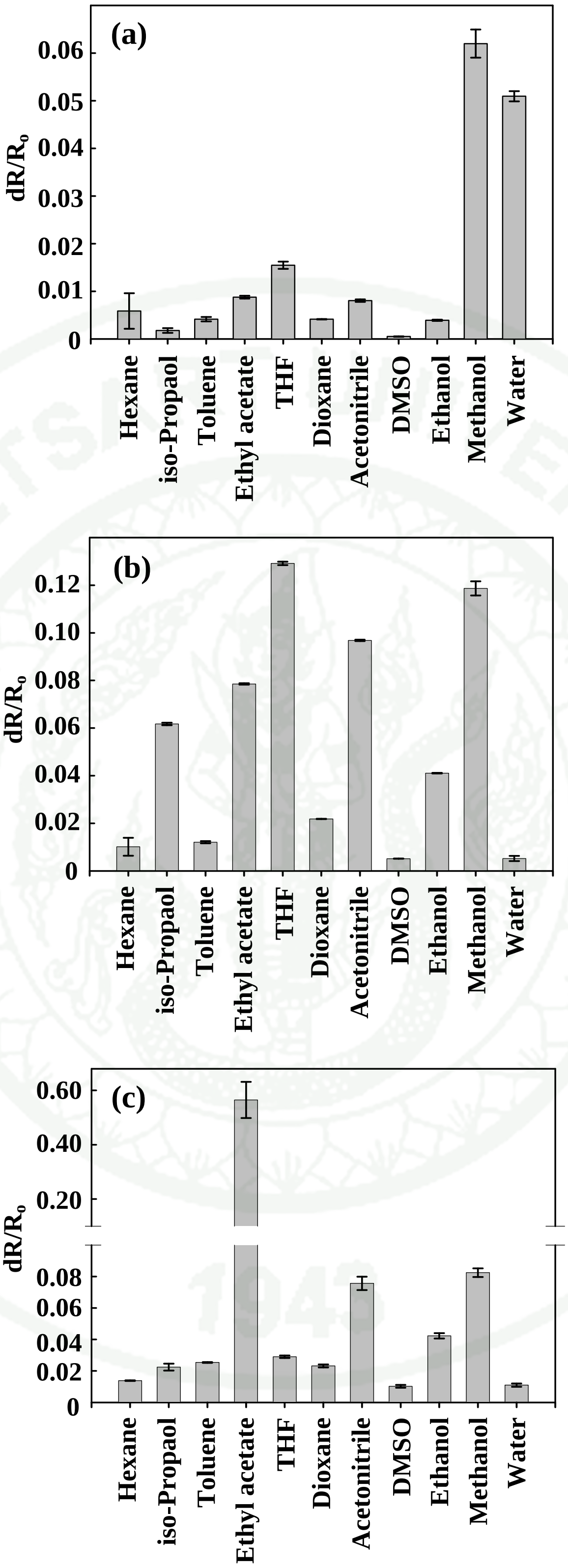


Figure 14 The electrical responses of composite films (a) 40% CB/PVA (b) 30% CB/PVA modified with benzoyl chloride (c) 30% CB/PVA modified with *p*-toluoyl chloride against solvent vapours.

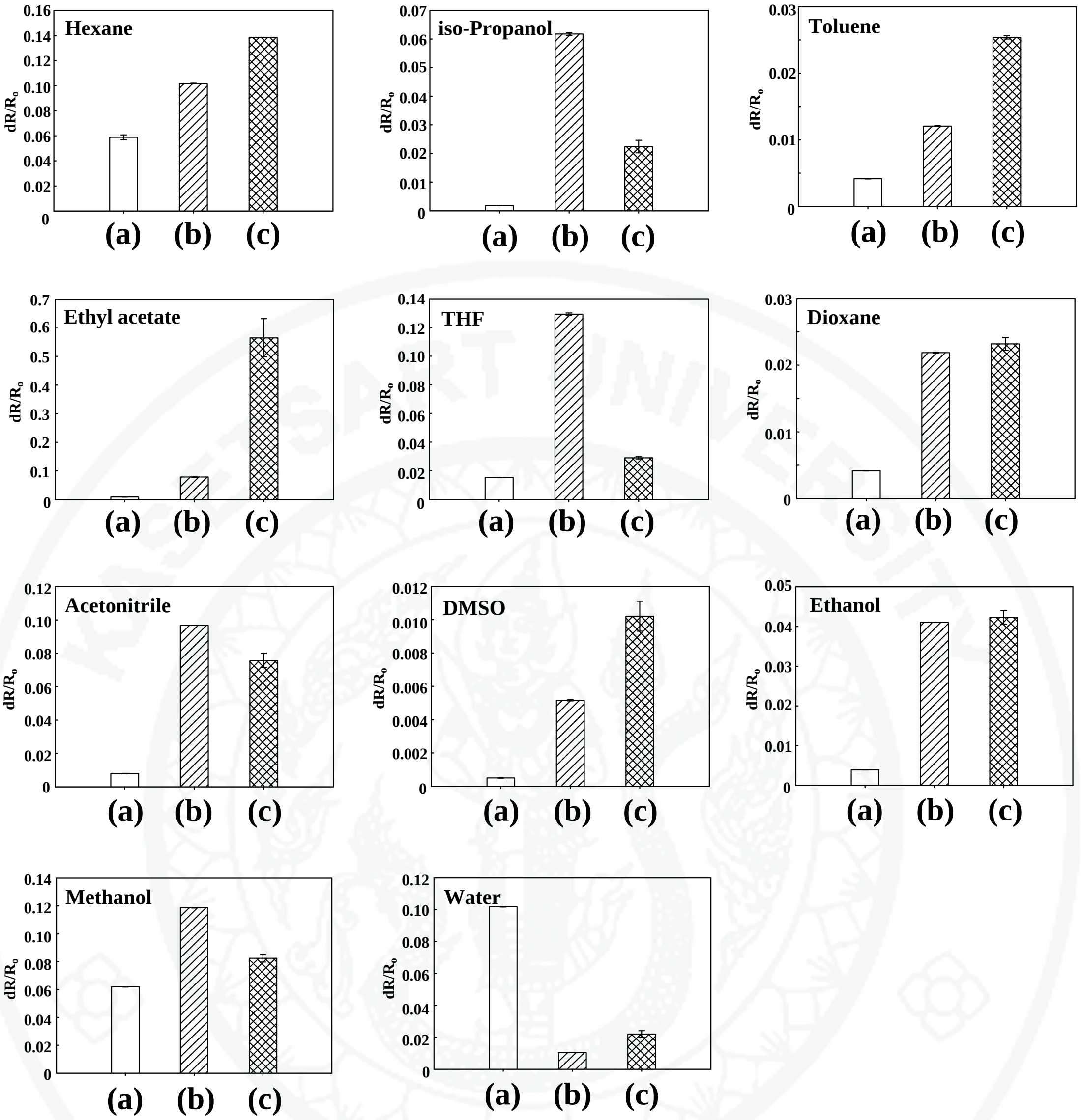


Figure 15 The comparison of the electrical responses of composite films between (a) 40% CB/PVA (b) 30% CB/PVA modified with benzoyl chloride (c) 30% CB/PVA modified with *p*-toluoyl chloride against solvent vapours.

When the polymer composites interact with the good solvent, the solvent using for polymer dissolving, the strong sensing signal was observed as shown in Figures 15. It was found that the 40% CB/PVA sensor clearly responded well to water while the 30% CB/PVA modified with benzoyl chloride sensor evidently responded well to iso-propanol, THF, acetonitrile, and methanol. In the case of the 30% CB/PVA modified with *p*-toluoyl chloride sensor, it clearly responded to hexane, toluene, ethyl acetate, dioxane, DMSO, and ethanol. The results indicated that the responsibility of each sensor depends on the chemical structures of poly(vinyl alcohol)s which were changed in polarity after modifying via esterification.

4.2. Repeatability

The previous section showed that the responsibility of the polymer composite films depended on the different saturated solvent vapour exposed. In this section, the repeatability of the polymer composite films was, then, discussed in term of the durability of the film. The repeatability of a sensor refers to how often a sensor can be operated under the same input conditions. The measurement output should be accurate by repeatedly use for long life of the sensor. In this work, the repeatability was observed from the electrical response of composite films recorded as a function of time in 5 cycles. The electrical resistance of composite films exposed to solvent vapours was, then, recorded as a function of time (Figure 16-18).

The repeatability of the composite films was investigated by the plot between resistivity and time of each solvent vapour which illustrate in term of baseline and peak height transforming (Figures 16-18). The electrical response of 40% CB/PVA composite film was shown in Figure 16. The baseline from the exposure of 40% CB/PVA composite film with hexane and toluene vapours was constant while the peak height was decreased (Figures 16(a) and (c)). It indicated that the composite film absorptivity was deteriorated due to solvent vapours exposure.

In the case of DMSO and ethanol vapours, the peak height of the 40% CB/PVA composite film was constant but the baseline was increased in each cycle of measuring (Figures 16(h) and (i)). The solubility strength of solvent vapour (DMSO and ethanol) is closely equal which exhibited the good interaction with the composite film. The composite film was still swollen by these solvent vapours although the film was purged with nitrogen gas before measuring in each cycle. The resistivity of films was, therefore, increasing as inspecting from the baseline of peaks.

In case of acetonitrile and methanol vapours (Figures 16(g) and (j)), the baseline slightly increased as comparing with the case of DMSO and ethanol vapours. It indicated that the interaction between the 40% CB/PVA composite film with acetonitrile and methanol was not so strong as the case of DMSO and ethanol.

In addition, it was found that both baseline and the height of peak were constant when it exposed to iso-propanol, ethyl acetate, THF, 1,4-dioxane, and water vapours (Figures 16(b), (d), (e), (f) and (k)). It means that the 40% CB/PVA composite film was durable in these solvent vapours without deterioration. The results implied that the 40% CB/PVA composite film was suitable for used as the sensor material for iso-propanol, ethyl acetate, THF, 1,4-dioxane, and water vapours.

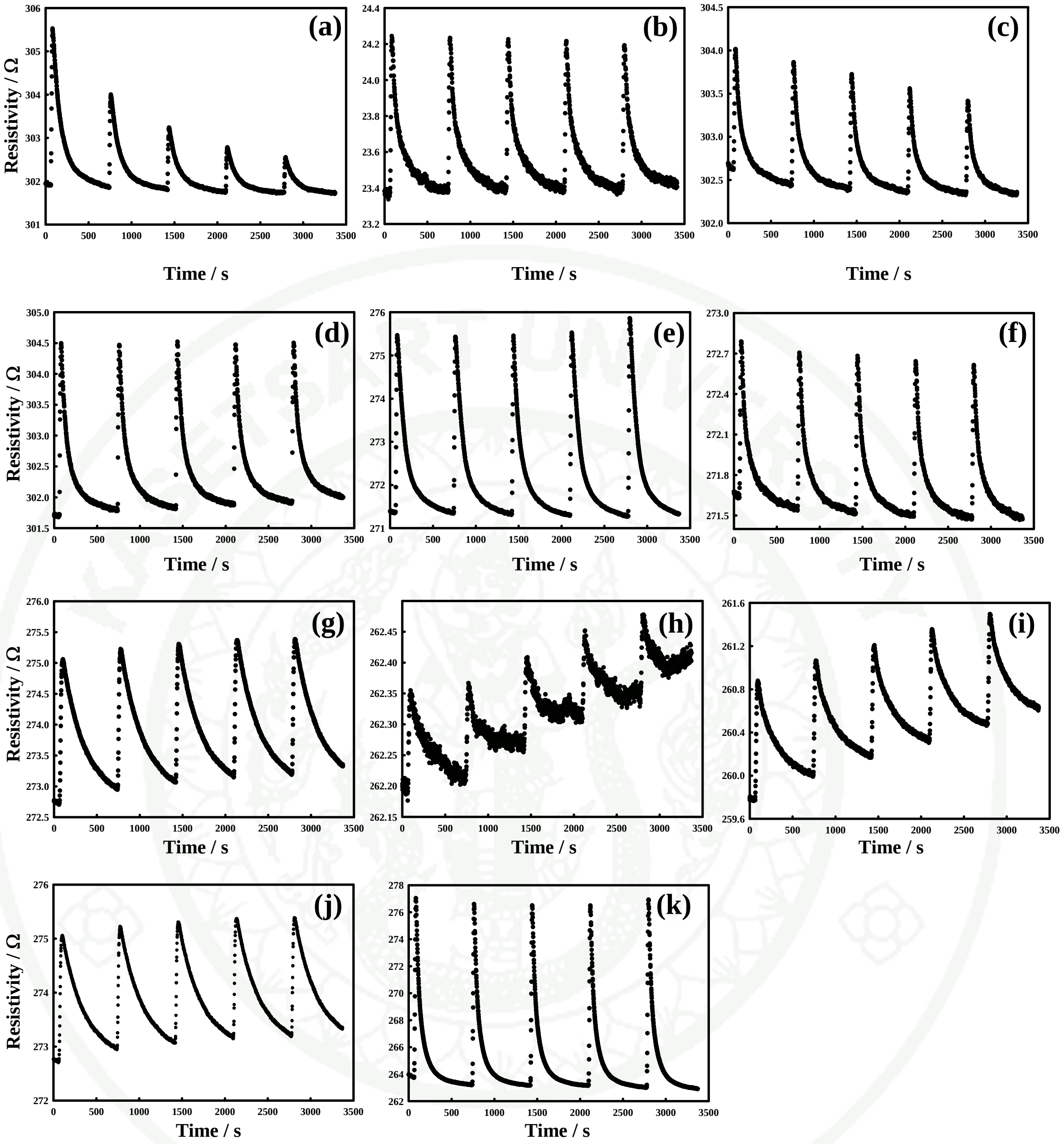


Figure 16 Typical electrical responses of 40% CB/PVA composite to various solvent vapours: (a) hexane, (b) iso-propanol, (c) toluene, (d) ethyl acetate, (e) THF, (f) 1,4-dioxane, (g) acetonitrile, (h) DMSO, (i) ethanol, (j) methanol, and (k) water.

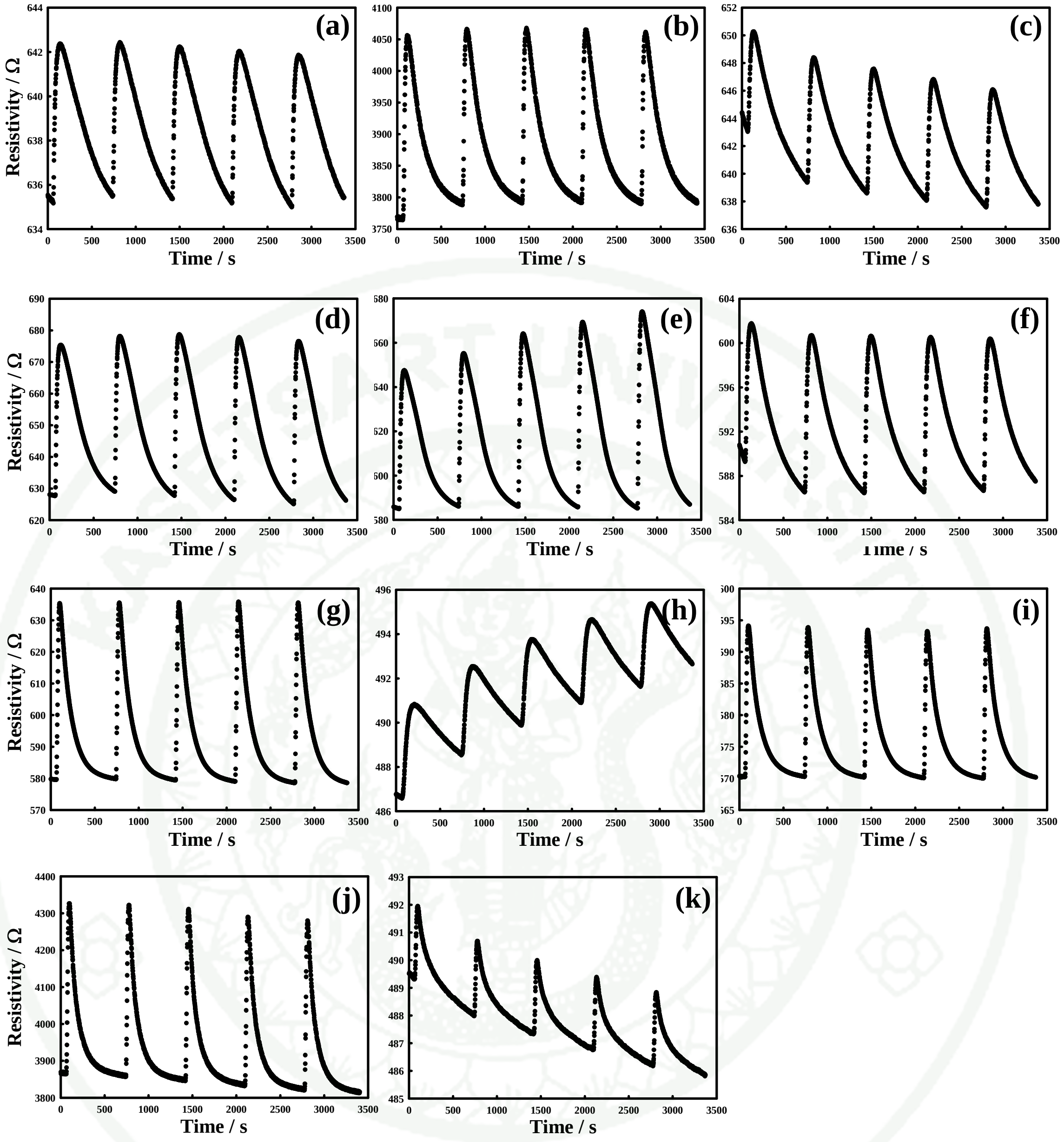


Figure 17 Typical electrical responses of 30% CB/PVA modified with benzoyl chloride composite to various solvent vapours: (a) hexane, (b) iso-propanol, (c) toluene, (d) ethyl acetate, (e) THF, (f) 1,4-dioxane, (g) acetonitrile, (h) DMSO, (i) ethanol, (j) methanol, and (k) water.

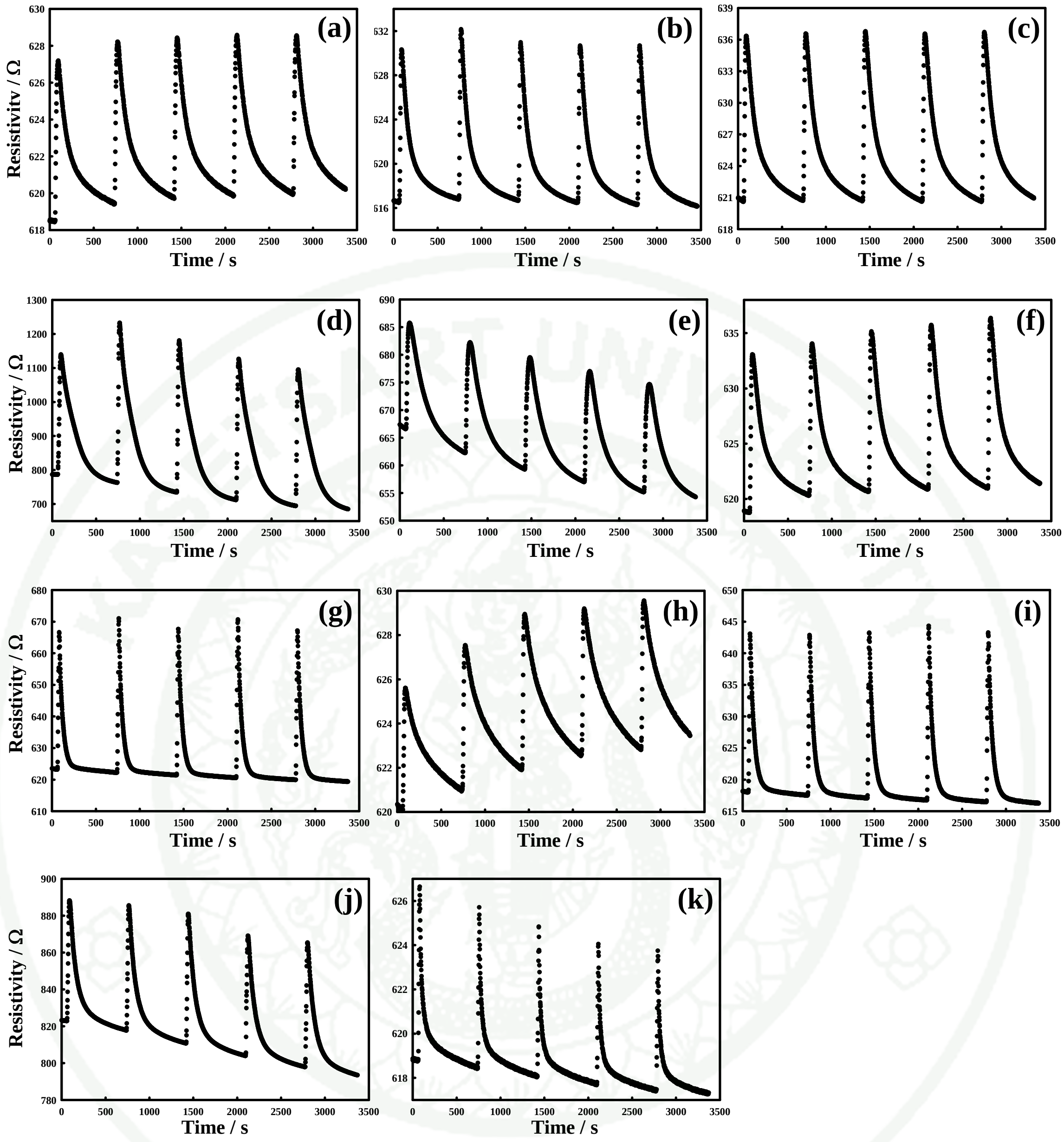


Figure 18 Typical electrical responses of 30% CB/PVA modified with *p*-toluoyl chloride composite to various solvent vapours: (a) hexane, (b) iso-propanol, (c) toluene, (d) ethyl acetate, (e) THF, (f) 1,4-dioxane, (g) acetonitrile, (h) DMSO, (i) ethanol, (j) methanol, and (k) water.

The results in Figures 17(c) and (k) showed the peak height was constant while the baseline decreased. The results indicated that toluene and water are the poor solvents for the 30% CB/PVA modified with benzoyl chloride. This film was, then, shrunk when it was exposed to toluene and water vapours resulting in decreasing in the resistivity.

Figure 17(h) showed that the peak height was constant while the baseline increased. It means that DMSO is the good solvent for the 30% CB/PVA modified with benzoyl chloride (Figure 15(h)). Moreover, the baseline and the height of peak were constant when the 30% CB/PVA modified with benzoyl chloride was measured in the conditions of hexane, iso-propanol, ethyl acetate, THF, 1,4-dioxane, acetonitrile, ethanol and methanol vapours (Figures 17(a), (b), (d), (e), (f), (g), (i), and (j)). The results indicated that the 30% CB/PVA modified with benzoyl chloride composite film was suitable for used as the sensor material since it was durable these solvent vapours without deterioration.

The results in Figure 18 implied that ethyl acetate, THF, methanol and water were the poor solvents (Figures 18(d), (e), (j) and (k)) while 1,4-dioxane and DMSO were the good solvents for the 30% CB/PVA modified with *p*-toluoyl chloride composite film. Additionally, the 30% CB/PVA modified with *p*-toluoyl chloride composite film was suitable for used as the sensor material since it was durable in hexane, iso-propanol, toluene, acetonitrile, and ethanol vapours without deterioration (Figures 18(a), (b), (c), (g), and (i)).

4.3. Sensitivity

There are various parameters affected to quality of sensor such as sensitivity, selectivity, accuracy, and precision, etc. The experiment was focus on sensitivity parameter which imply to the responsibility of the sensor to the analyte. Usually, the sensitivity can be defined as $[(R_{max}-R_o)/R_o]$ per concentration (ppm), where R_{max} stands for the maximum resistance of gas sensors in the reference gas (N_2 gas) containing target gases and R_o stands for the resistance in the reference gas. The polarity of synthetic compound was decrease by structural modification from PVA to PVA modified with benzoyl chloride and PVA modified with *p*-toluoyl chloride, respectively.

The sensitivity of 40% CB/PVA composite was decreased by order when detected with water, DMSO and methanol as shown in Figure 19(a). In the case of the modified poly(vinyl alcohol) composite films, they widely responded to various organic vapours. The highest sensitivity of 30% CB/PVA modified with benzoyl chloride composite was observed when detected with DMSO and iso-propanol, respectively as shown in Figure 19(b). The 30% CB/PVA modified with *p*-toluoyl chloride showed the high sensitivity to DMSO and ethyl acetate (Figure 19(c)).

From the above results indicated that those three composites responded to DMSO which affected from the substituent. The sensor of 40% CB/PVA modified with benzoyl chloride composite ($400x10^{-7}$) was increased 10 times from 40% CB/PVA composite while 30% CB/PVA modified with *p*-toluoyl chloride composite ($800x10^{-7}$) was increase 20 times from 40% CB/PVA composite. The water vapour was observed by using 40% CB/PVA composite as sensor.

From Figure 19, It showed that the sensitivity of the 30% CB/PVA modified with *p*-toluoyl chloride composite ($300x10^{-7}$) responded to ethyl acetate was increased 100 times when compared with 40% CB/PVA composite ($3x10^{-7}$). The increment of the sensitivity might be affected from the substituent on the PVA’s backbone.

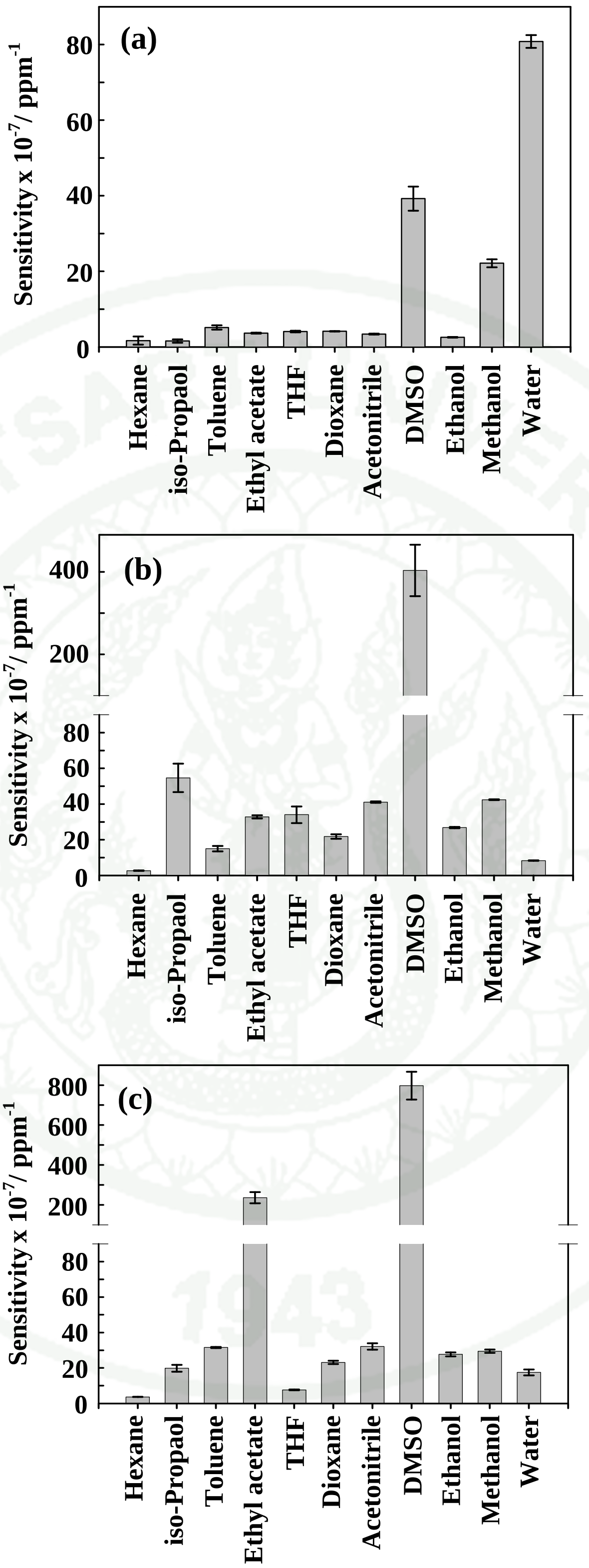


Figure 19 The sensitivity of (a) 40% CB/PVA (b) 30% CB/PVA modified with benzoyl chloride (c) 30% CB/PVA modified with *p*-toluoyl chloride composites exposed to various saturated solvent vapours.

CONCLUSIONS

The copolymers of poly(vinyl alcohol) were successfully prepared via esterification reaction by using two types of acid chlorides. The degree of esterification on PVA determined by FTIR, ^{1}H-NMR, and elemental analysis was found to be 50% when both acid chlorides; benzoyl chloride and *p*-toluoyl chloride were used. The unmodified and modified PVA provided various responses to various solvent vapours, they were, therefore, suitable to apply as the chemical vapour sensor materials in the future.

The present study was investigated the preliminary model of sensor using for DMSO and ethyl acetate vapour detection. Further study should be associated with the relationship between substituent and responsibility of polymer film.

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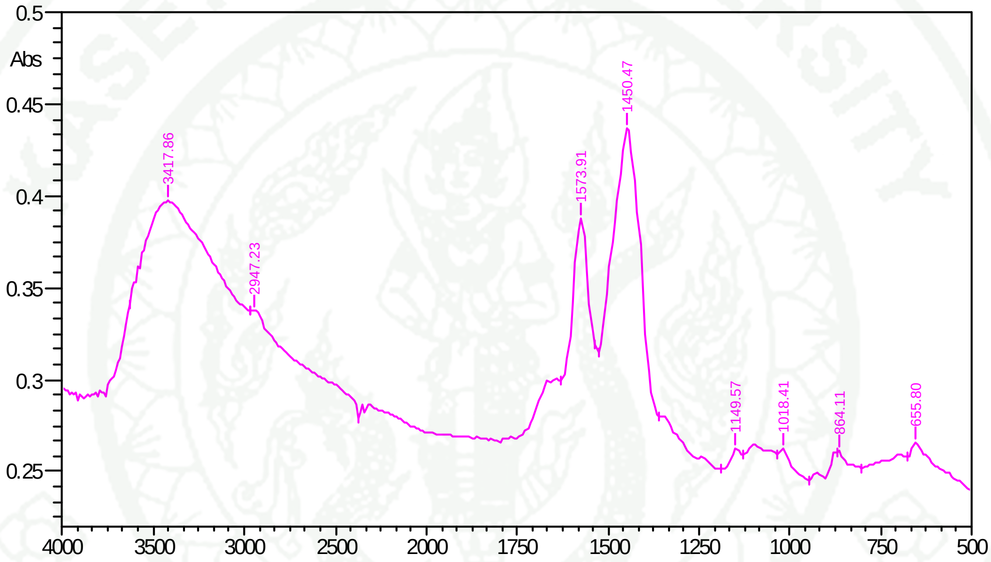
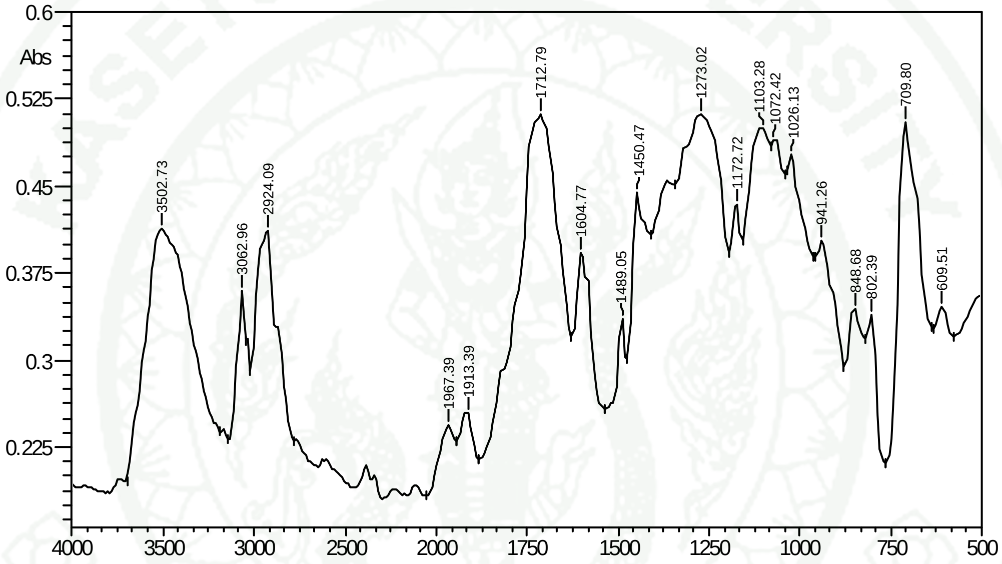
APPENDICES

Appendix A

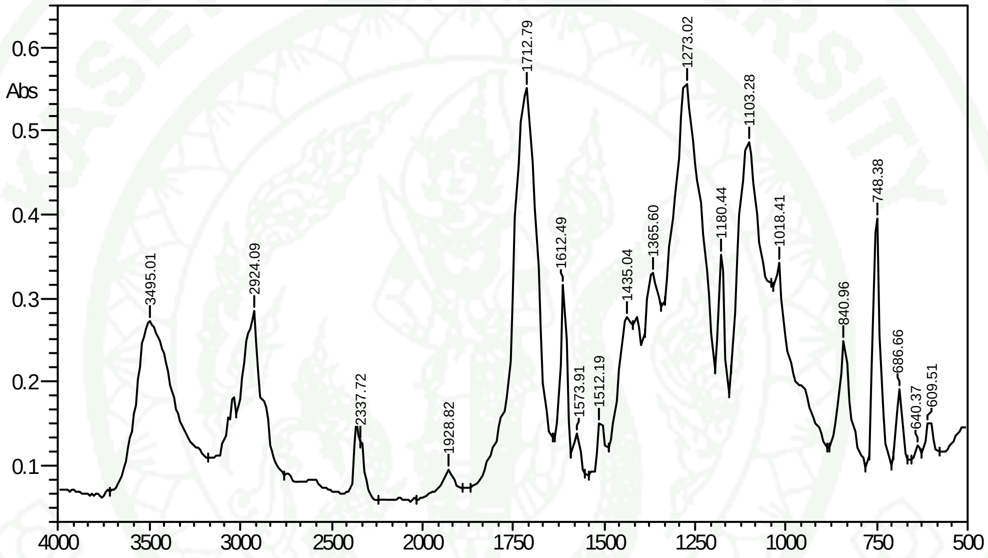
Raw data



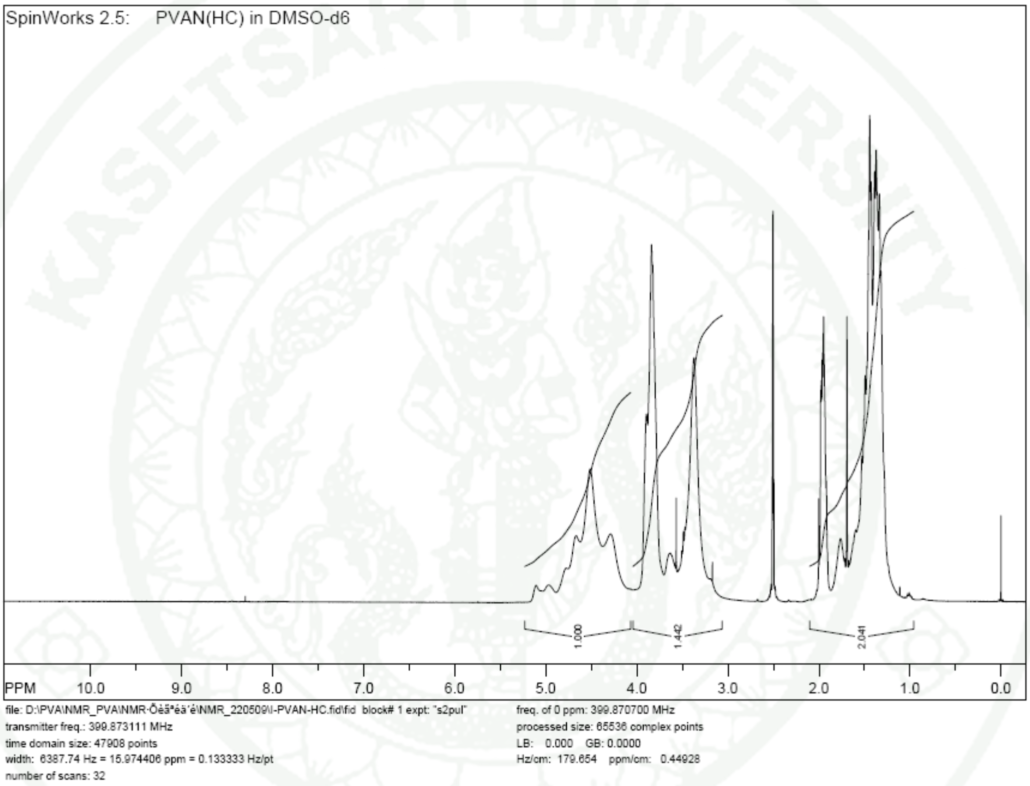
Appendix Figure A1 FTIR spectrum of poly(vinyl alcohol).



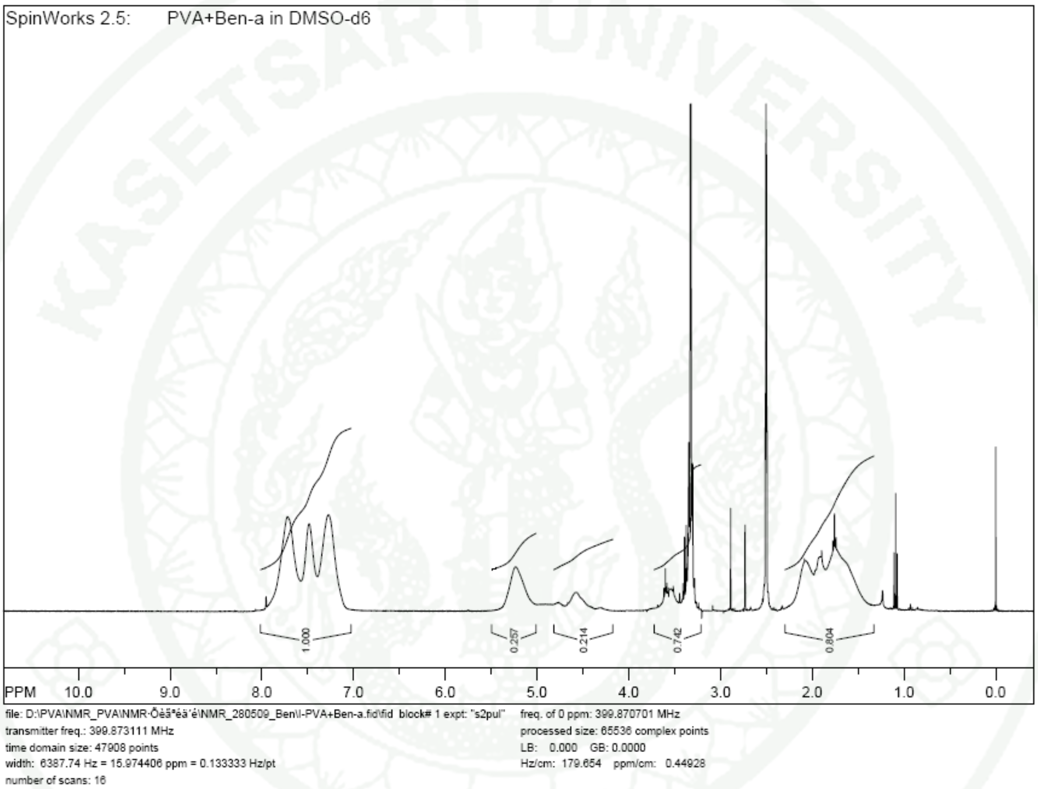
Appendix Figure A2 FTIR spectra of poly(vinyl alcohol) modified with benzoyl chloride.



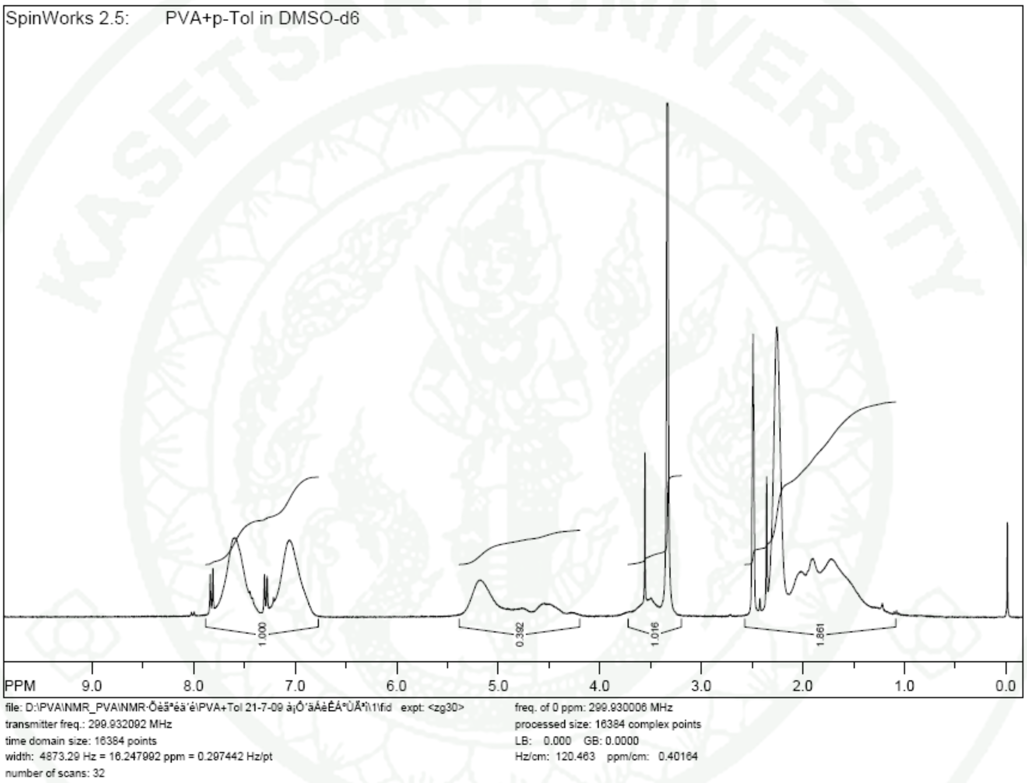
Appendix Figure A3 FTIR spectra of poly(vinyl alcohol) modified with *p*-toluoyl chloride.



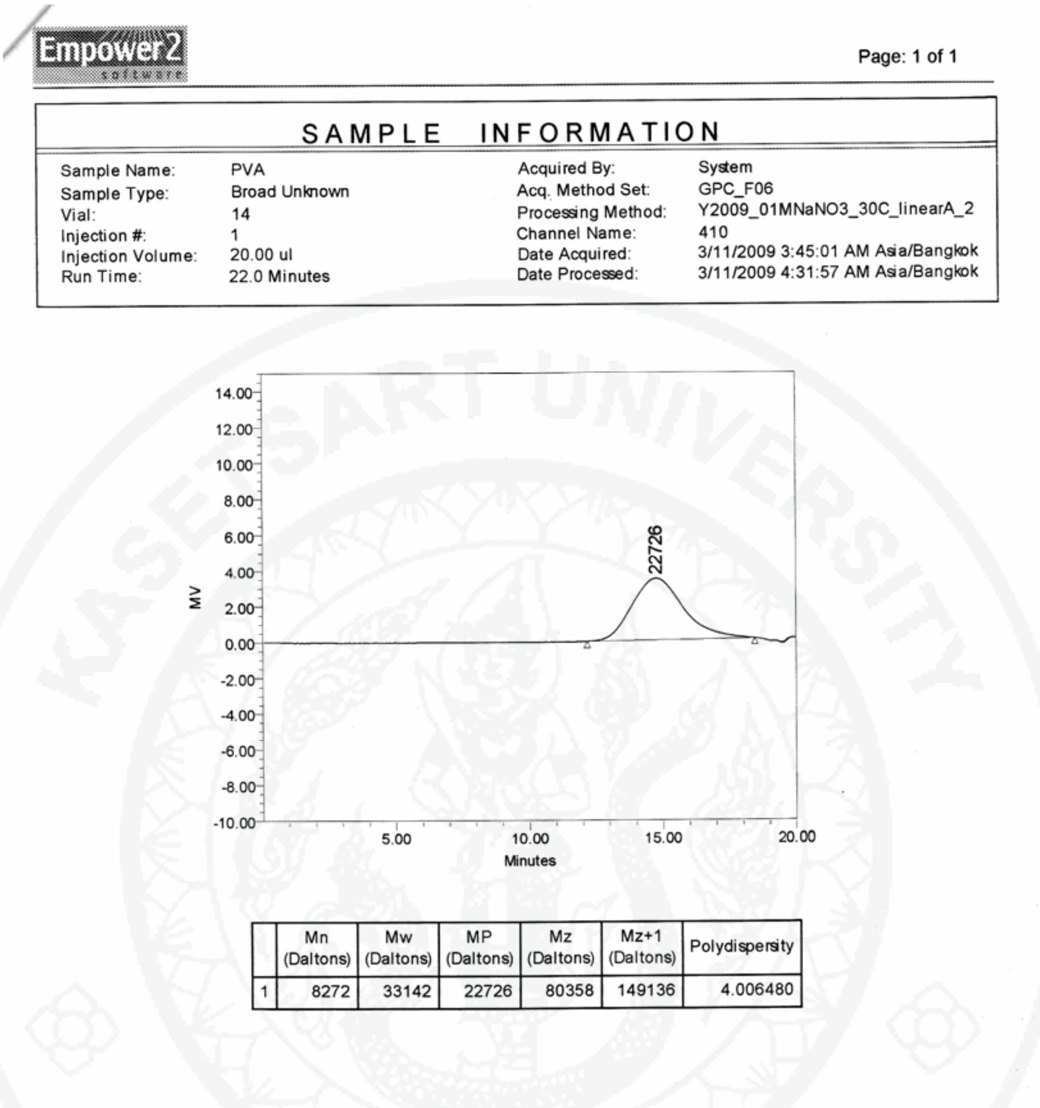
Appendix Figure A4 ^{1}H-NMR spectrum of poly(vinyl alcohol).



Appendix Figure A5 ^{1}H-NMR spectrum of poly(vinyl alcohol) modified with benzoyl chloride.



Appendix Figure A6 ^{1}H-NMR spectrum of poly(vinyl alcohol) modified with *p*-toluoyl chloride.



Empower2 software

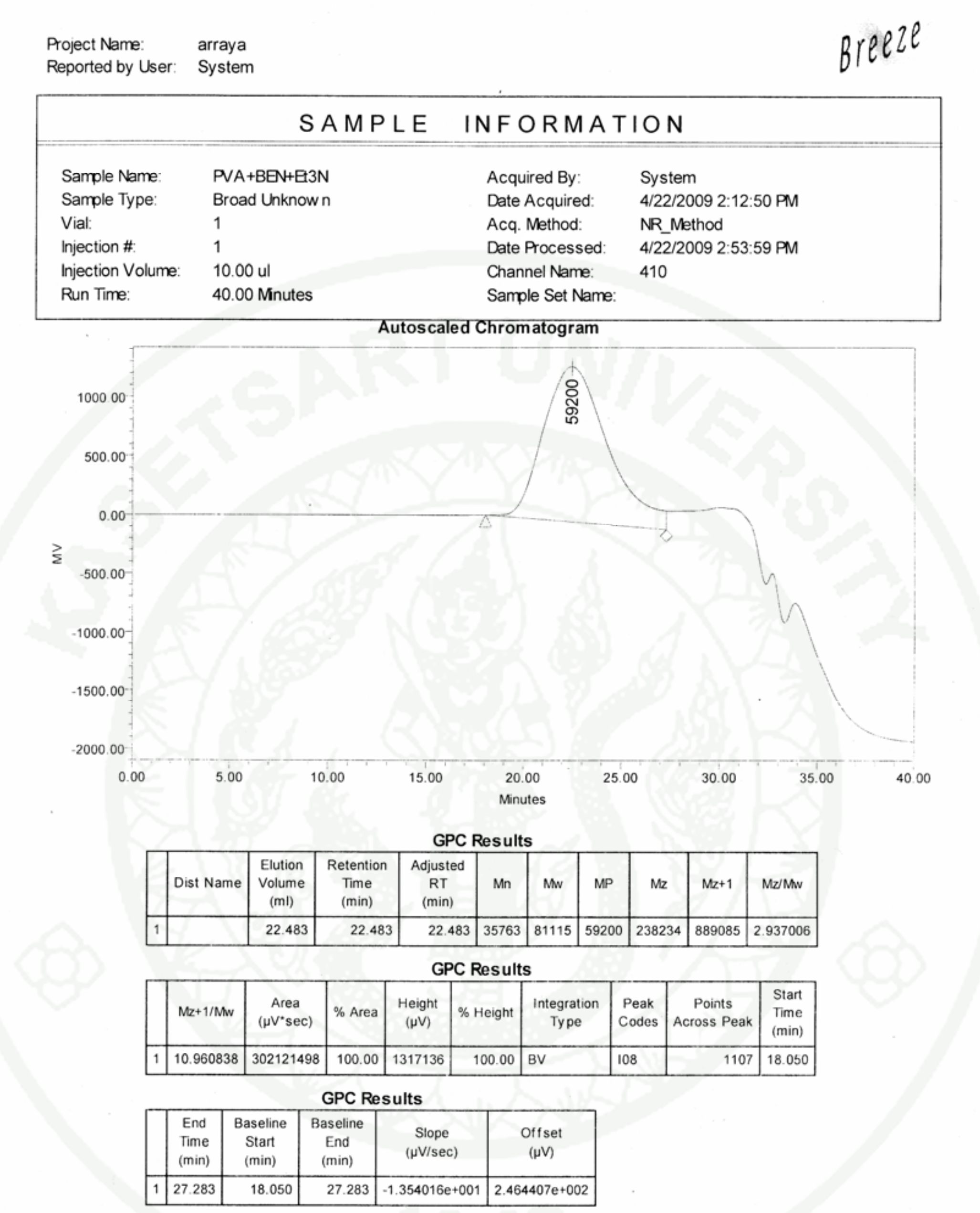
Page: 1 of 1

SAMPLE INFORMATION

Sample Name: PVA
Sample Type: Broad Unknown
Vial: 14
Injection #: 1
Injection Volume: 20.00 ul
Run Time: 22.0 Minutes
Acquired By: System
Acq. Method Set: GPC_F06
Processing Method: Y2009_01MNaNO3_30C_linearA_2
Channel Name: 410
Date Acquired: 3/11/2009 3:45:01 AM Asia/Bangkok
Date Processed: 3/11/2009 4:31:57 AM Asia/Bangkok

	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	8272	33142	22726	80358	149136	4.006480

Appendix Figure A7 GPC chromatogram of poly(vinyl alcohol).



Project Name: arraya
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	PVA+BEN+Et3N	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	4/22/2009 2:12:50 PM
Vial:	1	Acq. Method:	NR_Method
Injection #:	1	Date Processed:	4/22/2009 2:53:59 PM
Injection Volume:	10.00 ul	Channel Name:	410
Run Time:	40.00 Minutes	Sample Set Name:	

Autoscaled Chromatogram

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		22.483	22.483	22.483	35763	81115	59200	238234	889085	2.937006

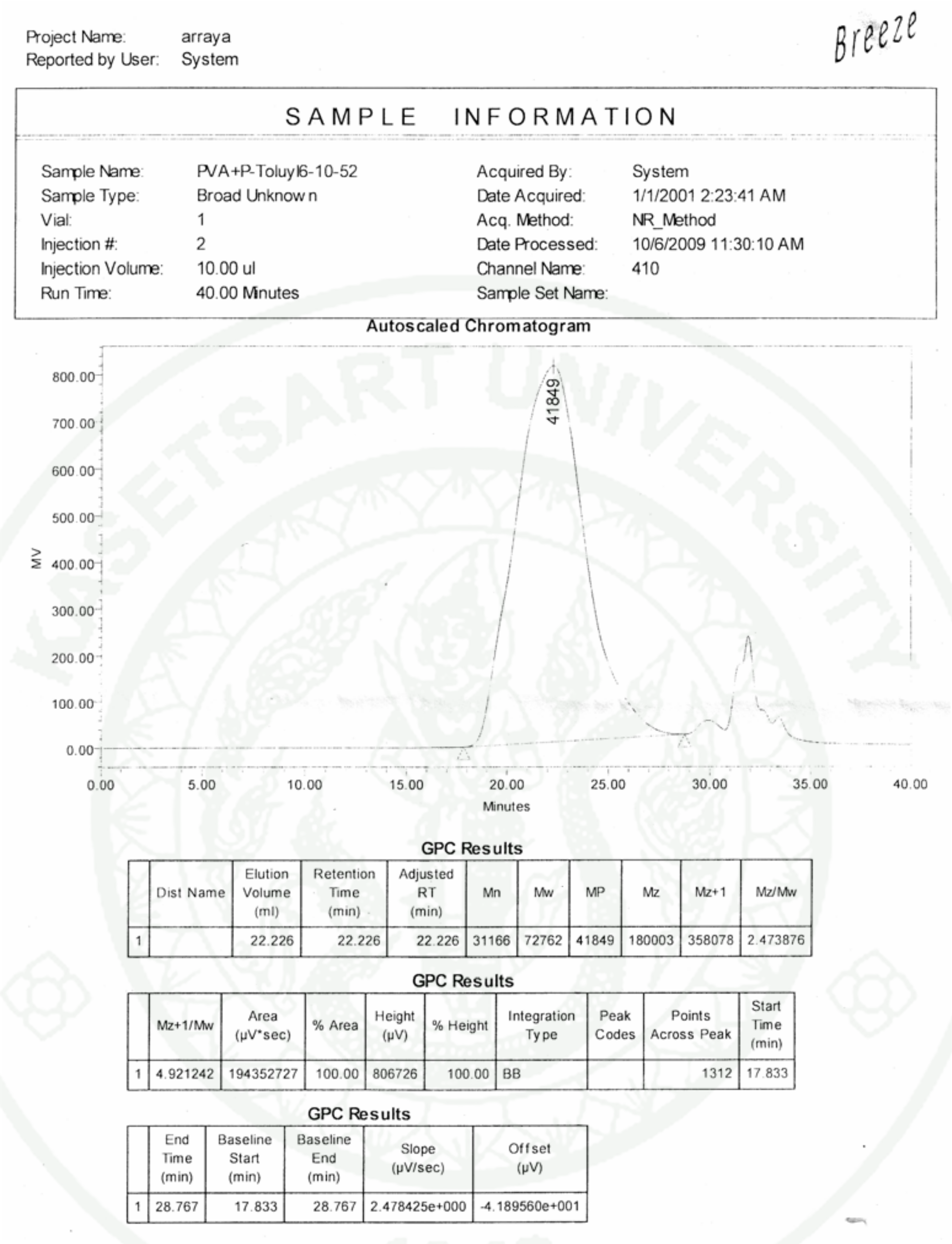
GPC Results

	Mz+1/Mw	Area (µV*sec)	% Area	Height (µV)	% Height	Integration Type	Peak Codes	Points Across Peak	Start Time (min)
1	10.960838	302121498	100.00	1317136	100.00	BV	I08	1107	18.050

GPC Results

	End Time (min)	Baseline Start (min)	Baseline End (min)	Slope (µV/sec)	Offset (µV)
1	27.283	18.050	27.283	-1.354016e+001	2.464407e+002

Appendix Figure A8 GPC chromatogram of poly(vinyl alcohol) modified with benzoyl chloride.



Project Name: arraya
Reported by User: System

Breeze

SAMPLE INFORMATION

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Sample Type:	Broad Unknown	Date Acquired:	1/1/2001 2:23:41 AM
Vial:	1	Acq. Method:	NR_Method
Injection #:	2	Date Processed:	10/6/2009 11:30:10 AM
Injection Volume:	10.00 ul	Channel Name:	410
Run Time:	40.00 Minutes	Sample Set Name:	

Autoscaled Chromatogram

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		22.226	22.226	22.226	31166	72762	41849	180003	358078	2.473876

GPC Results

	Mz+1/Mw	Area (µV*sec)	% Area	Height (µV)	% Height	Integration Type	Peak Codes	Points Across Peak	Start Time (min)
1	4.921242	194352727	100.00	806726	100.00	BB		1312	17.833

GPC Results

	End Time (min)	Baseline Start (min)	Baseline End (min)	Slope (µV/sec)	Offset (µV)
1	28.767	17.833	28.767	2.478425e+000	-4.189560e+001

Appendix Figure A9 GPC chromatogram of poly(vinyl alcohol) modified with *p*-toluoyl chloride.

Appendix B

Determination of vapour concentration

Vapour concentration was calculated by measuring the weight loss of solvent at room temperatures of 25 °C and atmospheric pressure of 1 atm. Each bottle loaded with 60 mL of each solvent was weighed before feeding carrier gas (N_2 gas) with the flow rate of 600 mL/min for 30 min. Each bottle was, then, weighed to obtain the weight loss of each solvent. Based on the ideal gas assumption, the weight loss of each solvent was converted to vapour concentration by using ideal gas equation ($PV = nRT$) while the temperature and the pressure were measured during proceeding the experiment. To confirm the reproducibility, the process of measuring weight loss was repeated twice.

The vapour concentrations of each solvent used for studied the responsibility of the composite films were calculated based on the ideal gas assumption and shown in Appendix Table B1. It was found that during 15 s, the concentration of each solvent vapour was varied and depended on the vapourized ability of each solvent. In addition, the results illustrated that the concentration of solvent vapours did not show any relationship to sensitivity of the composite films.

Appendix Table B1 Weight loss of each solvent after bubbling N_2 gas for 30 minutes

Solvent	**Molecular weight**	**Weight loss (g)**				**Concentration during 15 s (ppm)**
		1	**2**	**3**	**Average**	
Hexane	86.18	8.8974	8.6953	8.8569	8.8165	34,781
Toluene	92.14	2.2781	2.0832	2.1856	2.1823	8,052
iso-Propanol	60.06	2.0486	1.9557	1.9845	1.9963	11,300
THF	72.11	8.1569	8.0253	7.9868	8.0563	37,983
Ethyl acetate	88.11	6.3645	6.0949	6.1534	6.2043	23,939
1,4-Dioxane	88.11	2.6808	2.5175	2.6025	2.6003	10,033
Methanol	32.04	2.7319	2.6372	2.5406	2.6366	27,976
Ethanol	46.07	2.1188	2.0193	2.0851	2.0744	15,308
Acetonitrile	41.05	2.8681	2.8419	2.8312	2.8471	23,579
DMSO	78.13	0.0273	0.0320	0.0291	0.0295	128
Water	18.00	0.3461	0.3257	0.3296	0.3338	6,305

When $R = 0.0821\ \mathrm{L\cdot atm\cdot mol^{-1}\cdot K^{-1}}$
$T = 298.15\ \mathrm{K}$
$P = 1\mathrm{atm}$

Example of the calculation in the case of hexane

Ideal gas equation: $PV = nRT$

$$V = \frac{g}{Mw}\,\frac{RT}{P}$$

$$= \frac{8.8165}{86.18}\ \mathrm{mol} \times 0.0821\,\frac{\mathrm{L\cdot atm}}{\mathrm{mol\cdot K}} \times \frac{298.15}{1}\,\frac{\mathrm{K}}{\mathrm{atm}}$$

So, the volume of lost solvent after bubbling N_2 gas for 30 minutes (1800 s):

= 2.504 L or 2,504 mL

The flow rate of weight loss after bubbling N_2 gas for 30 minutes (1800 s):

$$\text{Flow rate} = \frac{2504}{1800}\frac{\text{mL}}{\text{s}}$$

$$= 1.391 \text{ mL/s}$$

If N_2 gas was bubbled to the bottle solvent for 15 seconds, the volume of lost solvent was:

$$= 20.87 \text{ mL/s}$$

The vapour concentration of solvent reached to test chamber was:

$$= \frac{20.87}{600}\frac{\text{mL/s}}{\text{mL/s}} \text{ x } 10^6$$

$$= 34{,}781 \text{ ppm}$$

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