PREPARATION AND CHARACTERIZATION OF SILVER DOPING IN TiO_2/PVA-PTFE NANOCOMPOSITES SOL SOLUTION

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ABSTRACT

TiO_2/PVA nanocomposites were synthesized by sol-gel technique by using TiO_2 and polyvinyl alcohol as starting materials. PVA was varied from 0.1 – 0.5 wt%. Titanium loaded was also varied from 5 – 9 ml. The hightest degree of transparent was obtained. Titanium increased photocatalytic activity of nanocomposites. Glacial acitic acid was used to adjust the stable solution which various pH from 2 – 4. Polytetrafluoroethylene or Teflon was added to improve lubricity, hydrophobic and friction properties. 6 – 8 ml of Teflon were tested. Optically transparent sol solutions were obtained. Silver was used as an additive to improve the performance of sol solution. Teflon with 5 – 9 ml was examined. The best condition of nanocomposites was investigated which is 0.3 wt% of PVA, 5 ml of Titanium solution, and 7 ml of Teflon at pH 2.5. In order to understand the bonding between molecules, FT-IR and UV-Vis characterizations of nanoconposites were performed. Comparison of the spectra clearly shows the polymeric structure of Titanium in PVA structure. The limited amount of silver was added at 2 wt%. FT-IR spectra showed that bonding of Ag-PVA is not stable or not strong enough to stabilize the compound means Silver cannot replace Titanium in TiO_2/PVA nanocomposites. The absorbance of UV-Vis spectra increased with adding silver. Comparison of the spectra was discussed in term of the polymeric structure of Titanium, Teflon and Silver in PVA structure.

Keywords : TiO_2/PVA-PTFE nanocomposites, Ag-TiO_2 nanocomposites, sol solution

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Miss Siriluck Ngammee

Miss Nattamas Wanichpan

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Chapter 1

Introduction

1.1 Motivation

The antibacterial effects of silver (Ag) salts have been known for over 2000 years, but they have only been in common use as an antimicrobial since the 19th century. Ag is currently used to control bacterial growth in a variety of applications, including dental work, catheters, and burn wounds [1]. Ag ions and Ag-based compounds are highly toxic to microorganisms. They show strong biocidal activity against as many as 12 species of bacteria including E. coli [2]. Silver nanoparticles have proved to be most effective as it has good antimicrobial efficacy against bacteria, viruses and other eukaryotic micro-organisms [3]. It has been shown that reducing the particle size of materials is an efficient and reliable tool for improving their actions [4]. In fact, nanotechnology helps to overcome the limitations of size and can change the outlook of the world regarding science [5].

Titanium dioxide is a potent photocatalyst that can breakdown almost any organic compound, upon exposure to UV light in aqueous medium. These methods usually require the cost-competitive techniques and expensive devices in those application areas for film deposition. Sol–gel process is one of the most common methods used for producing photocatalytic TiO_2 material in the form of powder or coatings. During the process, two highly reactive species are formed, hydroxyl radicals $OH^{\cdot}$, and superoxide ions O_2^{-} [6]. Hydroxyl radicals are very strong oxidizing agents and can destroy organic materials including, those that make up living cells. Titanium dioxide and TiO_2^{-} composites can achieve a complete bacterial killing process within a few hours. It has been reported that microorganisms such as Staphylococcus, Bacillus subtilis, Escherichia coli, algae marine, fungi, and virus are inactivated using irradiated TiO_2.

Silver-TiO_2 nanocomposites destroy or deactivate pathogenic microorganisms resulting in the inhibition of their growth and reproduction. This antimicrobial silver-TiO_2 inorganic material offers several advantages such as high chemical stability, re-usage, and in particular the use of expensive oxidizing agents is not necessary to carry out the photodegradation. Moreover, the silver particles can maintain its metallic state under continuous UV irradiation. The immobilization of these antimicrobial materials, on polymers, glass, membranes and foams has been reported previously.

However, the deposition of silver–TiO_2 as a film coating is an important issue to be satisfactory resolved.

Polyvinyl alcohols (PVA) are synthetic polymers used since the early 1930s in a wide range of industrial, commercial, medical and food applications including resins, lacquers, surgical threads and food-contact applications. Polyvinyl alcohol (PVA) has multiple applications, such as sizing process of the textile industry and paper coating due to its high tensile strength, better flexibility, high thermal and chemical stability, water-soluble and the good film-forming capability. PVA was chosen as a protective polymer because it has the desired solution properties in water and it contains many isolated hydroxyl functional groups, which can adsorb and complex with metal ions. PVA is relatively insoluble in organic solvents and its solubility in aqueous solutions is adaptable to its necessary application.

The aims of this work are to find the maximum loaded of silver in polymeric matrix and therefore creating possibility of the application in sol solution. Ag–TiO_2 sol solution was prepared from sol-gel method. Here, we report the microstructure of as-prepared Ag– TiO_2 sol solution by FT-IR and UV-Vis spectrometry techniques. Mainly, the bondings in modified polymer of Ag–TiO2 are also investigated.

1.2 Objectives

- To standardize the appropriate proportion for the Silver doping in PVA/TiO_2 to be Ag-TiO_2 nanocomposites sol solution.
- To prepare polymeric matrix of Ag-TiO_2 composites in PVA matrix.
- To characterize the bonding structure of TiO_2-Ag nanocomposites by FT-IR and UV-Vis spectrometry techniques.

1.3 Scope of study

1. Literature review was conducted to gain the background knowledge and recent development in the relevant areas.

2. Study the replacing of Silver in polymer matrix, properties of TiO_2 nanocomposites solution, and photocatalytic properties of Ag–TiO_2 nanocomposites.

3. Study the preparation and characterization of Ag-TiO_2 composites.

4. Prepare polymeric matrix of TiO_2 and Ag-TiO_2 composites in PVA matrix.

5. Varies Ti, Teflon, pH and Ag ratios.

6. Indicate the best condition for the most transparent modified polymer.

7. Characterization by using FTIR and UV-Visible spectrometer.

1.4 Expected Results

1.4.1 Obtain Ag-TiO_2/PVA-Teflon nanocomposites sol solution.

1.4.2 Obtain the appropriate condition for synthesis Ag-TiO_2/PVA-Teflon nanocomposites.

Chapter 2

Theoretical Backgrounds and Literature Reviews

2.1 Silver

Silver has been known since ancient times that silver and its compounds are effective antimicrobial agents. Legendary examples include the use of diluted solution of silver salts in the prophylactic treatment of newborn eye infections and in the treatment of burn wounds. Currently, silver-containing agents are regularly used in clinical wound dressings (e.g., silver sulfadiazine) as well as in the coatings of biomedical materials (e.g., silver impregnated catheters).

A number of chemical forms of silver are known to exhibit antimicrobial activities. The Ag^+ ions in the form of a silver nitrate solution are the prototypical antimicrobial silver species. The biocidal effect of Ag^+, with its broad spectrum of activity including bacterial, fungal, and viral agents, can be achieved at submicromolar concentrations. In addition, tarnished bulk silver has also been reported to be antimicrobial, ascribed to its surface oxide layer and/or release of Ag (I) species. Novel composite materials for the delivery of biocidal Ag^+ ions are continuously being developed.

Another antimicrobial silver species that has been known for a long time, but has received little attention, is the nanometer-sized silver particles (silver nanoparticles, nano-Ag). However, the recent advances in research on metal nanoparticles appear to revive the use of nano-Ag in various biomedical applications. Nano-Ag prepared by a variety of synthetic methods has been shown to be effective antimicrobial agents. For example, wound dressings based on sputtered nano-Ag are employed in clinical practice to suppress microbial infection in burn wounds. Recently, our group also demonstrated that nano-Ag synthesized by borohydride reduction exhibit cytoprotective activities toward human immunodeficiency virus-1 infected cells.

The antimicrobial modes of action of Ag^+ ions have been known in some details. Micromolar levels of Ag^+ ions have been reported to uncouple respiratory electron transport from oxidative phosphorylation, inhibit respiratory chain enzymes, or interfere with the membrane permeability to protons and phosphate. In addition, higher concentrations of Ag^+ ions have been shown to interact with cytoplasmic components and nucleic acids. As for nano-Ag, recent electron microscopic studies have revealed that the majority of nano-Ag was localized in the membranes of treated *E. coli* cells, while some penetrated into the cells. However, the biochemical and molecular aspects of the actions of this distinct silver species have never been directly addressed. [25]

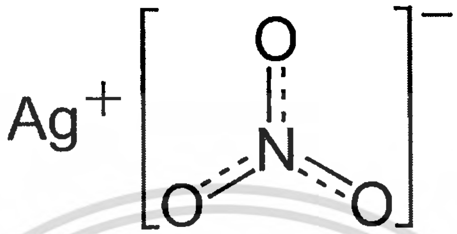


Figure 2.1 Chemical structure of Silver nitrate

2.2 Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) is one of the materials of interest for decomposition of environmental pollutants, i.e., to diminish the serious and detrimental effects of air or water pollution. TiO_2 is nontoxic, and is able to oxidize various compounds under irradiation of UV lights such as part of sunlight wavelength. A lot of studies for the photo decomposition of pollutants by these photocatalysts are carried out, and the preparation of highly active photocatalysts has been studied. In our previous study, TiO_2 thin film photocatalysts, were prepared by dip coating with the sol-gel method using a water vapor in air for the hydrolysis of metal alkoxide, and these films effectively photooxidized nitrogen oxides. They showed a large specific surface area, excellent transparency, good crystallinity, and high photocatalytic activity. However, this preparation method had the following problems. First, more than 20 dip coatings were needed to obtain 1 μm thick films. Second, this process could be operated only under low humidity conditions. In order to obtain sufficient film thickness with only a few dip coating times, a highly viscous solution would be required. Previous studies in sol-gel method, control of the solution viscosity was reported by the control of the hydrolysis of metal alkoxide and polymerization of sol. However, it is difficult to control the solution viscosity in the sol-gel reaction, since solution viscosity is easily changed depending on several complete factors, i.e., temperature, humidity, reaction time, mixing ratio of reagents, etc. Viscosity can be controlled by adding other components to the system, if they are miscible and do not react with the other components in the system. We have found that a highly viscous solvent, α-terpineol, successfully gives a fine and transparent thin film photocatalyst. This solvent is suitable for dip coating, since it does not react with metal alkoxide and has a good affinity to glass substrate. Moreover, the thin films do not show any clacks and flaking off from substrate after calcination in spite of the thick films obtained. It is expected that the dip coating time can be reduced significantly by using this solvent. [18]

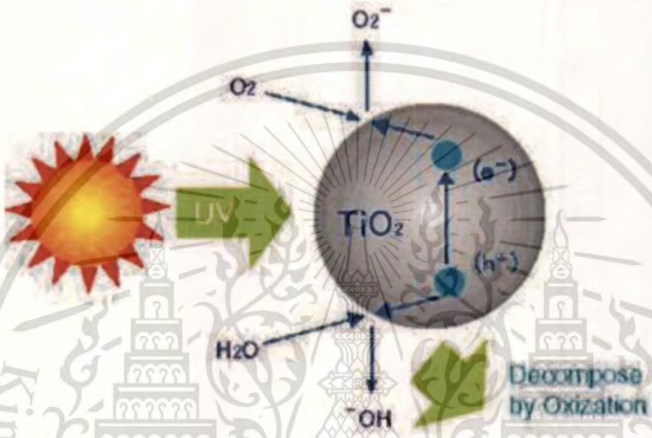


Figure 2.2 Photocatalytic of Titaniun Dioxide

2.3 Polyvinyl alcohol

PVOH, PVA, or PVAl are a water-soluble synthetic polymer. Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer, will then reduce its tensile strength, but increase its elongation and tear strength. PVA is fully degradable and dissolves quickly. PVA has a melting point of 230°C and 180–190°C (356-374 degrees Fahrenheit) for the fully hydrolyzed and partially hydrolyzed grades, respectively. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. PVA is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it. PVA is close to incompressible. The Poisson's ratio has been measured to between 0.42 and 0.48. [17]

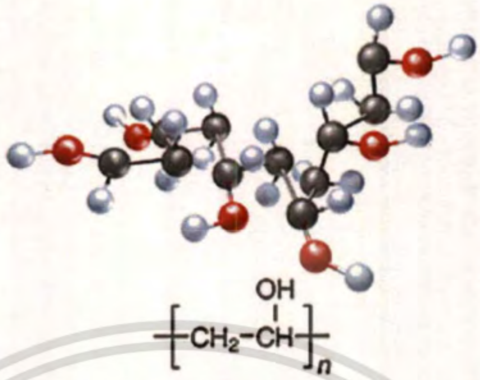


Figure 2.3 Functional group of Polyvinyl alcohol (PVA)

2.4 Teflon

Polytetrafluoroethylene (PTFE) is a synthetic material accidentally invented in the late 1930s while a chemist was endeavoring to develop a new type of perfluorethylene-based refrigerant. Rather than achieving a chlorofluorocarbon, the scientist was surprised to find that the perfluorethylene used in the process reacted with the iron content of its container and polymerized under pressure. Less than a decade later, this new material was being distributed on a commercial scale and was eventually patented under the name Teflon®. However, it would be another 20 years before PTFE would hit the frying and become known as the first non-stick coating for cookware. In fact, this material was used for a variety of other purposes at first. [26]

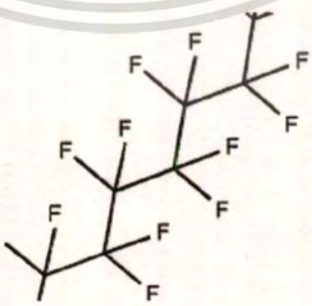


Figure 2.4 Structure of Teflon $(C_2F_4)_n$

2.5 Titanium (IV) Isopropoxide ($TiOR_4$)

Titanium isopropoxide reacts with water to deposit titanium dioxide:

$Ti(OCH(CH_3)_2)_4 + 2\ H_2O \rightarrow TiO_2 + 4\ (CH_3)_2CHOH$

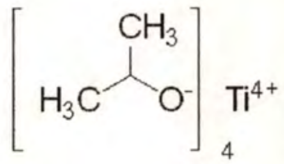


Figure 2.5 Titanium Isopropoxide Chemical Formula

This reaction is employed in the sol-gel synthesis of TiO_2 based materials. Typically water is added to a solution of the alkoxide in an alcohol. The nature of the inorganic product is determined by the presence of additives (e.g. acetic acid), the amount of water, and the rate of mixing.

Titanium isopropoxide is a component of the Sharpless epoxidation, a method for the synthesis of chiral epoxides. It is an alkoxide of titanium (IV) and appears as a liquid that is colorless to light yellow in form. Its odor is similar to Isopropyl Alcohol. It is a powerful reducing agent and water-and-air-reactive. It is highly flammable and fumes in air. Its vapors are heavier than air. It is soluble in water. It decomposes quickly in water forming inflammable Isopropyl Alcohol. It is a strong reducing agent and reacts quickly and dangerously with oxygen and other oxidizing agents. [19]

2.6 Sol-gel

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. The sol-gel process may be described as: “Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.” A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid. A gel consists of a three dimensional continuous network, which encloses a liquid phase. In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric substructure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by Van Der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved with a large variety of functionality have been studied intensively. The combination of the two components at a molecular level would provide novel properties that are hardly obtained from conventional organic or inorganic materials. It results, for instance, in waveguides, optical biosensors or thermally stable nonlinear optical materials. The homogeneous combination of two materials also produces an enhancement of the mechanical strength of organic polymers such as poly(dimethylsiloxane) with silica particles or a modification of the mechanical properties of silica by introduction of organic polymers into the silica phase. The hybrid materials are also potential candidates for catalysts and gas separation membranes. The sol–gel technique applied to metal alkoxides is one of the most efficient methods for the preparation of composite materials. The method comprises initial hydrolysis of those metal alkoxides and subsequent condensation and removal of the solvents, resulting in metal oxides.

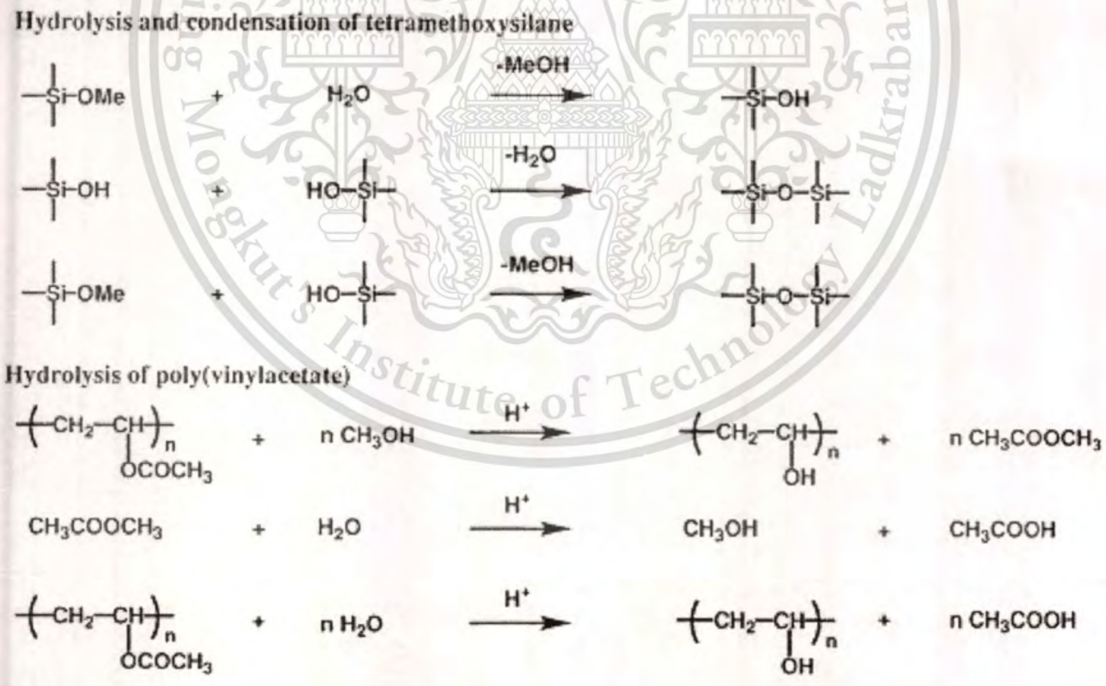


Figure 2.6 Top: Conventional sol–gel technique for preparing composite materials.

Bottom: PVAc hydrolysis.

The advantage of the sol–gel technique for preparing composite materials is the low reaction temperature, e.g. room temperature, at which the reactions are conducted, while the conventional melt fusion technique of silica glasses needs a high temperature. Thus, it enables the incorporation of organic elements into inorganic materials without deterioration of their functionality. It is also noteworthy that silica gels obtained by the sol–gel reaction contain a large number of residual hydroxyl groups. [24]

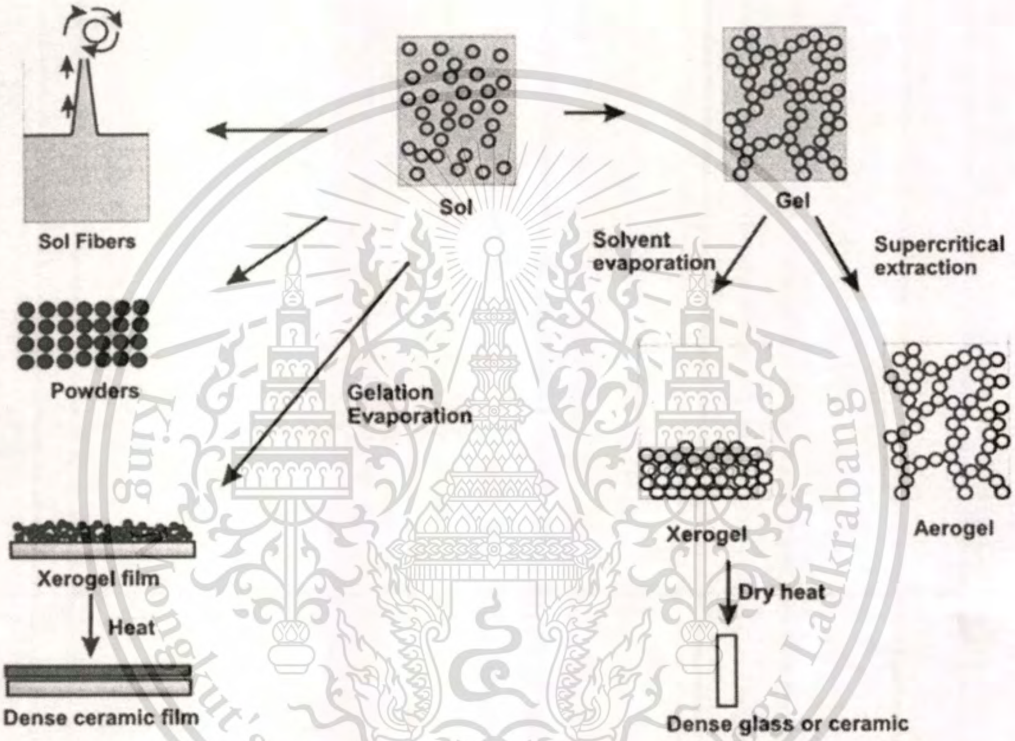


Figure 2.7 Sol-gel processing option

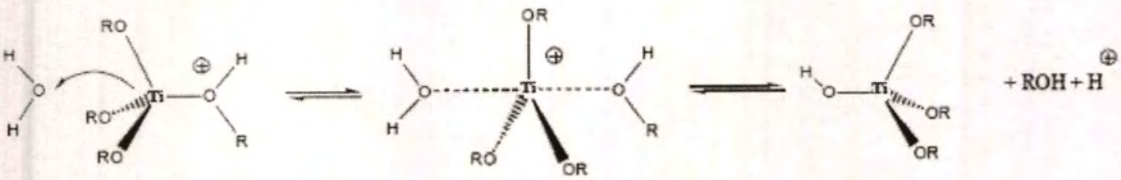
<u>Acidic conditions</u>:

Reaction rate decreases as more alkoxy groups are hydrolyzed reaction at terminal Si favored, linear polymer products, fibers RSi(OR)3 more reactive than Si(OR)4 Sol-Gel Methods.

<u>Basic conditions</u>:

Reaction rate increases as more alkoxy groups are hydrolyzed reaction at central Si favored, branched polymer products, spherical particles, powders RSi(OR)3 less reactive than $Si(OR)_4$.

Acid catalysed hydrolysis



Base catalysed hydrolysis

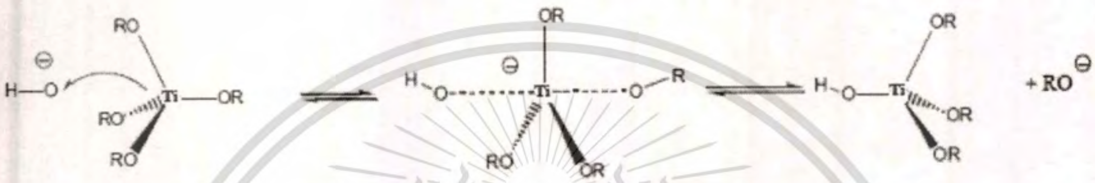


Figure 2.8 Sol-Gel Methods

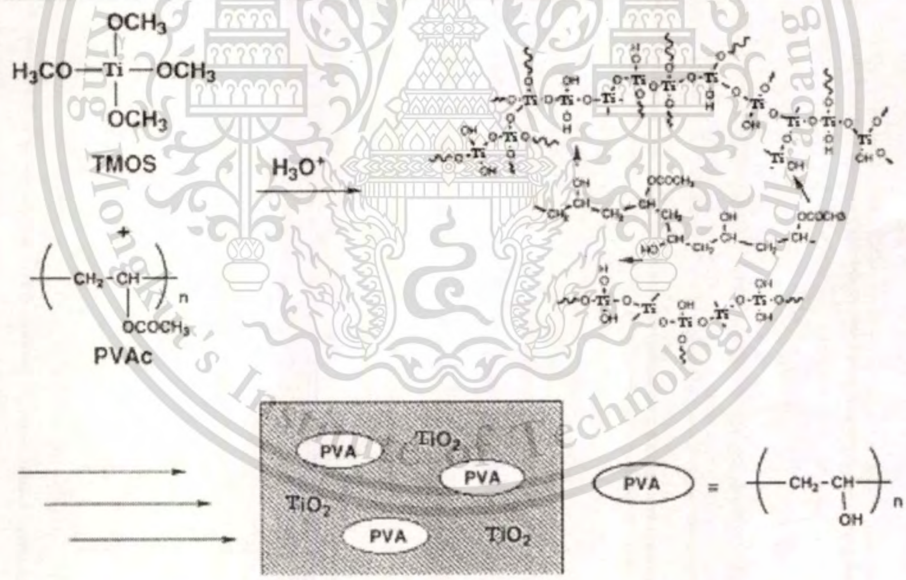


Figure 2.9 Preparation of polymer hybrids.

2.7 Antibacterial

An antibacterial is a compound or substance that kills or slows down the growth of bacteria. The term is often used synonymously with the term antibiotic(s); today, however, with increased knowledge of the causative agents of various infectious diseases, antibiotic(s) has come to denote a broader range of antimicrobial compounds, including anti-fungal and other compounds. Many antibacterial products for cleaning and hand-washing are sold today. Such products do not reduce the risk for symptoms of viral infectious diseases in otherwise healthy persons. This does not preclude the potential contribution of antibacterial products to reducing symptoms of bacterial diseases in the home.

2.8 Characteristic Analysis Techniques

2.8.1 FTIR

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

Qualitative Analysis

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular *"fingerprint"*. While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

Quantitative Analysis

Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses. Usually these are rather simple types of tests in the concentration range of a few ppm up to the percent level. For example, EPA test methods 418.1 and 413.2 measure the C-H absorption for either petroleum or total hydrocarbons. The amount of silica trapped on an industrial hygiene filter is determined by FTIR using NIOSH method 7602.

Physical Principles

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)]. The energy corresponding to these transitions between molecular vibration states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Sample Preparation

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification. Solutions can also be analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which can be filled with liquid, such as the extract for EPA 418.1 analysis. This creates a longer path length for the sample, which leads to increased sensitivity. Sampling methods include making a mull of a powder with hydrocarbon oil (Nujol) or pyrolyzing insoluble polymers and using the distilled pyrolyzate to cast a film. Matrials can be placed in an Attenuated Total Reflectance (ATR) cell and gases in gas cells.

FTIR-Microscope

For small samples or samples with surface contamination visible to the naked eye, a microscope attachment can be used to obtain reflectance or transmittance spectra on particles as small as 20 microns.

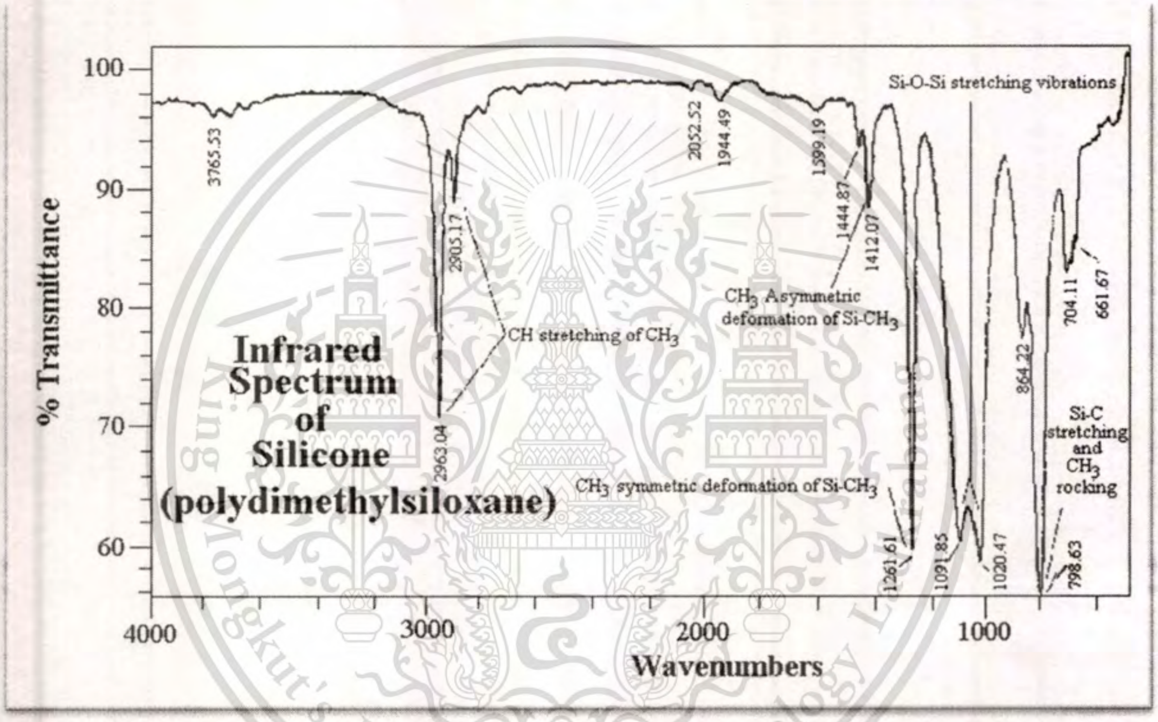


Figure 2.10 An example of FTIR-Infrared Spectrum result

2.8.2 Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis)

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, *b*, and the concentration, *c*, of the absorbing species. *Beer's Law* states that

A = ebc, where **e** is a constant of proportionality, called the *absorbtivity.*

Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. For example, the absorption that is observed in the UV region for the carbonyl group in acetone is of the same wavelength as the absorption from the carbonyl group in diethyl ketone.

Experimental Procedure

The following simulation illustrates the procedures for making spectrophotometric measurements.

First, the intensity of light (I_0) passing through a blank is measured. The intensity is the number of photons per second. The blank is a solution that is identical to the sample solution except that the blank does not contain the solute that absorbs light. This measurement is necessary, because the cell itself scatters some of the light.

Second, the intensity of light (I) passing through the sample solution is measured. (In practice, instruments measure the power rather than the intensity of the light. The power is the energy per second, which is the product of the intensity (photons per second) and the energy per photon.)

Third, the experimental data is used to calculate two quantities: the transmittance (T) and the absorbance (A).

$$T = I / Io$$

$$A = -\log_{10} T$$

The transmittance is simply the fraction of light in the original beam that passes through the sample and reaches the detector. The remainder of the light, $1 - T$, is the fraction of the light absorbed by the sample. (Do not confuse the transmittance with the temperature, which often is given the symbol T.)

In most applications, one wishes to relate the amount of light absorbed to the concentration of the absorbing molecule. It turns out that the absorbance rather than the transmittance is most useful for this purpose. If no light is absorbed, the absorbance is zero (100% transmittance). Each unit in absorbance corresponds with an order of magnitude in the fraction of light transmitted. For $A = 1$, 10% of the light is transmitted ($T = 0.10$) and 90% is absorbed by the sample. For $A = 2$, 1% of the light is transmitted and 99% is absorbed. For $A = 3$, 0.1% of the light is transmitted and 99.9% is absorbed.

Using the simulation below, perform the following steps:

- Measure the intensity of light passing through the blank.
- Measure the intensity of light passing through the sample.
- Calculate the transmittance.
- Calculate the absorbance.

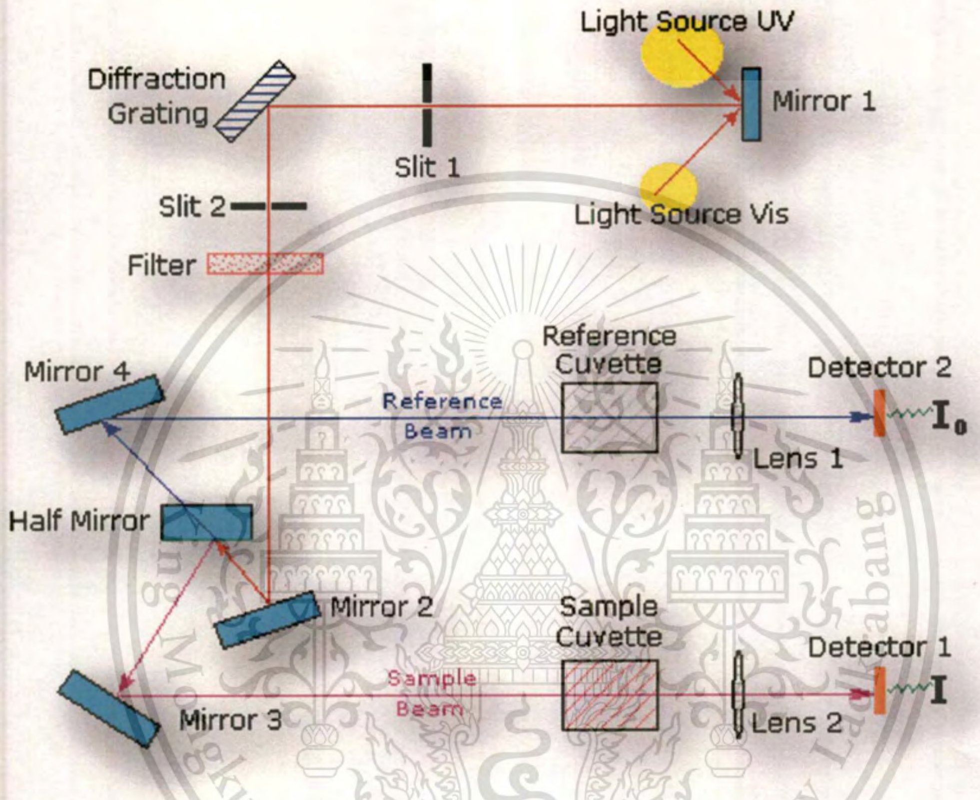


Figure 2.11 Show the simulation of UV-Vis or UV/Vis

2.9 Literature reviews

Studied of Chun-Nam Lok, Chi-Ming Ho, Rong Chen, Qing-Yu He, Wing-Yiu Yu, Hongzhe Sun, Paul Kwong-Hang Tam, Jen-Fu Chiu, and Chi-Ming Che (2006) found that nano-Ag and Ag^+ ions in the form of $AgNO_3$ appear to share a similar membrane-targeting mechanism of action. The effective concentrations of nano-Ag and Ag^+ ions are at nanomolar and micromolar levels, respectively. Nano-Ag appears to be significantly more efficient than Ag^+ ions in mediating their antimicrobial activities. [7]

The studied of S. Honary, K. Ghajar, P. Khazaeli and P. Shalchian found that the antimicrobial effect of silver nanoparticles strongly depends on their size. Smaller particles showed greater antimicrobial activity than bigger one. [8]

It was observed by S.-H. Nam, S.-J. Cho, C.-K. Jung, J.-H. Boo, J. Šícha, D. Heřman, J. Musil, J. Vlček (2011) that the TiO2 films prepared by the sol–gel method are amorphous and the water contact angle α decreases with increasing time of UV irradiation more rapidly than that on the anatase TiO_2 film prepared by reactive magnetron sputtering. [9]

Chunbao Xu, Amyn S. Teja (2008) showed that the presence of PVA during particle formation is an effective way to obtain narrow particle size distributions. The presence of PVA during synthesis hinders particle aggregation, and thereby results in uniform particles and narrow particle size distributions. In addition, our results show that the average particle size decreases with increasing PVA concentration when the residence time is of the order of 2 s, and becomes nearly independent of PVA concentration when the residence time is 10 s or higher. [10]

Chapter 3

Experiment

3.1 Chemicals

- PVA ; Polyvinyl Alcohol 10%wt. (MW = 70000-80000)
- Titanium iso-propoxide, 98+%
- Teflon ; Polytetrafluoroethylene (PTFE)
- Silver Nitrate, 99.88%
- Absolute Ethanol
- Gracial Acetic acid, free aldehyde
- Distilled Water

3.2 Apparatus

- Volumetric flask-100ml
- Beaker-250 ml
- Beaker-100 ml
- Buret-10 ml
- Dropper
- Pipet-10 ml
- Rubber bulb
- Stirrer with hot plate
- Magnetic bar
- Clamp
- pH-meter
- Distilled bottle
- Watch glass

3.3 Characterizations

- FTIR : Fourier transform infrared spectroscopy
- UV-Vis : Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry

3.4 Methodology

1. Preparation of PVA solution (0.1, 0.2, 0.3, 0.4, 0.5 %wt)

1.1 Weigh PVA (MW 70.000-80,000) as 0.1, 0.2, 0.3, 0.4, and 0.5 g in sequence.

1.2 Dissolve each of them with 50 ml of distilled water.

1.3 Heat at 60°C and stir with magnetic stirrer until clear solution is obtained (about 1 hr).

1.4 Pour in to 100 ml volumetric flasks and adjust volume to 100 mL with distilled water.

2. Ultrasonic irradiation

2.1 Adjust ultrasonic irradiation bath with 70°C of distilled water and keep it warming.

2.2 Put volumetric flasks of PVA solutions into ultrasonic irradiation bath.

2.3 Sonicate them for 30 minutes.

3. Preparation of TiO_2 stock solution

3.1 Mix 5 ml of glacial acetic acid with 25 ml of absolute ethanol in beaker.

3.2 Stir it with magnetic stirrer for 15 minutes.

3.3 Keep stirring and slowly add 5 ml of Ti-isopropoxide as dropwise to beware the precipitation.

3.4 Pour the solution into 100 ml volumetric flask and adjust the volume with absolute ethanol (99%).

4. Preparation of TiO_2/PVA

4.1 Specify the optimum concentration of PVA

4.1.1 Mix 1 ml of TiO_2 stock solution with various amount of PVA solutions (0.1, 0.2, 0.3, 0.4, and 0.5 wt%)

4.1.2 Observe the solutions which one is the clearest solution without precipitate.

4.1.3 Use the concentration of PVA in the clearest one as the optimum concentration of PVA.

4.2 Specify the optimum amount of TiO_2 stock solution

4.2.1 Add TiO_2 stock solution into 100 ml-volumetric flask as 5.0, 6.0, 7.0, 8.0 and 9.0 ml in sequence.

4.2.2 Adjust with the PVA solution which is the optimum concentration of PVA (part 4.1.3).

4.2.3 Observe the solutions which one is the clearest solution without precipitate.

4.2.3 Use amount of TiO_2 in the clearest one as the appropriate amount of TiO_2 stock solution.

5. pH adjustment

5.1 Prepare the most stable PVA solution as resulted from part 4.1.3.

5.2 Adjust PVA solution with difference pH ranges which are 2.0, 2.5, 3.0 3.5 and 4.0 by using glacial acetic acid.

5.3 Add the appropriate amount of TiO_2 stock solution (part 4.2.3) into 100 ml-volumetric flask.

5.4 Adjust volume with PVA solution which are difference pH ranges (2.0, 2.5, 3.0 3.5 and 4.0).

5.5 Observe physical changing to find the clearest solution.

5.6 Use pH of the clearest one as the appropriate pH range.

6. Specify the optimum amount of Teflon

6.1 Prepare the most stable PVA solution with appropriate pH from part 5.6.

6.2 Add the appropriate amount of TiO_2 stock solution (part 4.2.3) into 100 ml-volumetric flask.

6.3 Add Teflon as 0.60, 0.65, 0.70, 0.75 and 0.80 ml in sequence.

6.4 Adjust volume with PVA solution which is the appropriate pH range.

6.5 Observe physical changing to find the clearest solution without precipitate.

6.6 Use amount of Teflon in the clearest one as the appropriate amount of Teflon.

7. Preparation of Ag stock solution

7.1 Prepare the most stable PVA solution with appropriate pH from part 5.6.

7.2 Weigh $AgNO_3$ – Silver Nitrate as 2, 4, 6, 8 and 10 g in sequence.

7.3 Dissolve each of them with 50 ml of PVA solution which is the most stable.

8. Preparation of Ag-TiO_2 /PVA-PTEF

8.1 Prepare the most stable PVA solution with appropriate pH from part 5.6.

8.2 Add the appropriate amount of TiO_2 stock solution (part 4.2.3) into 100 ml-volumetric flask.

8.3 Add Ag stock solutions from part 7.3 into 100 ml-volumetric flask in sequence.

8.4 Observe physical changing and characterization with UV-Visible spectrophotometer for 5 days to study transfiguration of Ag in solution.

9. Characterization

9.1 Characterize the structure of solution by FTIR spectrometer.

9.2 Characterize UV absorbance by UV-Visible spectrophotometer to study transfiguration of solution.

3.5 Flow diagram

Preparation of PVA solution (0.1, 0.2, 0.3, 0.4, 0.5 %wt)

Dissolve PVA in distilled water by heat it up to 60°C and stir with magnetic stirrer until the clear solution is obtained (about 1 hr).

↓

Ultrasonic irradiation

Put the PVA solutions into ultrasonic irradiation bath and sonicate them at 70°C for 30 mins.

↓

Preparation of TiO_2 stock solution

Mix 5 ml of glacial acetic acid with 25 ml of absolute ethanol in beaker and stir it for 15 mins.

Add 5 ml of Ti-isopropoxide as dropwise.

Pour it into 100 ml volumetric flask and adjust volume by absolute ethanol

↓

Specify the optimum concentration of PVA

Mix 1 ml TiO_2 solution with various amount of PVA solutions (0.1, 0.2, 0.3, 0.4, and 0.5 wt%) .

Observe and fix the concentration of PVA in the clearest one as the optimum concentration of PVA.

↓

Specify the optimum amount of TiO_2 stock solution

Add Ti solution into 100 ml-volumetric flask as 5.0, 6.0, 7.0, 8.0 and 9.0 ml and adjust with stable PVA solution

Observe and fix amount of TiO_2 in the clearest one as the appropriate amount of TiO_2 stock solution.

↓

pH adjustment

Adjust the stable PVA solution with difference pH ranges which are 2.0, 2.5, 3.0 3.5 and 4.0 by acetic acid.

Add the appropriate amount of Ti solution into 100 ml-volumetric flask and adjust volume with PVA solution.

Observe and fix pH of the clearest one as the appropriate pH range.

Specify the optimum amount of Teflon

Add the appropriate amount of TiO_2 stock solution into 100 ml-volumetric flask.

Add Teflon as 0.60, 0.65, 0.70, 0.75 and 0.80 ml in sequence.

Adjust volume with PVA solution which is the appropriate pH range.

Observe physical changing to find the clearest solution without precipitate.

Preparation of Ag stock solution

Weigh $AgNO_3$ – Silver Nitrate as 2, 4, 6, 8 and 10 g in sequence and dissolve each of them with 50 ml of the stable PVA solution

Preparation of Ag-TiO_2 /PVA-PTEF

Add the appropriate amount of TiO_2 solution into 100 ml-volumetric flask and add Ag stock solutions.

Observe physical changing and characterization with UV-Visible spectrophotometer for 5 days.

Characterization

Characterize the structure of solution by FTIR spectrometer and characterize UV absorbance by UV-Visible spectrophotometer to study transfiguration of solution.

Chapter 4

Results and Discussions

Polyvinyl alcohol (PVA) is a synthetic water-soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. Functional group of PVA is an electron pair donor or Lewis base. Ionic cross-linking may be achieved by introducing metal ions into an acid-containing adhesive or by generating acid/base interaction between polymer chains. Chemical cross-linking is a highly versatile method to create and modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability. The occurrences of cross-linked between long chain help stabilize metal. Ti was inserted between long chain PVA polymers. The certain amount of Ti metal loaded was demanded. Overloaded Ti metal will terminate the propagation process of chain growth polymerization. It causes the agglomeration of short chain. Some Ti metal was hydrolyzed to be metal oxide with lower stability, unstable complexes. Improper cross-linked complexes of short chains will decrease the tendency of dissolving. This will make the solution turbid and precipitate later on.

4.1 Degree of transparent

Figure 4.1 Physical observed by necked eyes of crosslinked in sol solutions

In this research involved with the preparation and characterization of PVA, Titanium dioxide nanocomposites and the improvement of solution properties using Teflon as additive agent with various ratios. Effect of Titanium ratio, Teflon contents and solution appearances on physical and chemical properties was studied.

The solutions was ordered as 5 degree of transparent when 1 is represent to the clearest solution and 5 is represent to the most opaque solution.

Figure 4.2 Comparison of different concentration of PVA mixed with 1 ml of TiO_2 stock solution

Table 4.1 Degree of transparent with different concentration of PVA mixed with 1 ml of TiO_2 stock solution

Concentration of PVA	Degree of transparent
PVA 0.1% wt.	3
PVA 0.2% wt.	2
PVA 0.3% wt.	1
PVA 0.4% wt.	4
PVA 0.5% wt.	5

When 1 refers to the clearest solution and 5 refers to the most opaque solution.

Figure 4.3 Comparison of different amount TiO_2 stock solution with 0.3 wt% of PVA

Table 4.2 Degree of transparent with different concentration of PVA mixed with 1 ml of TiO_2 stock solution

Concentration of TiO_2	**Degree of transparent**
5 ml of TiO_2	1
6 ml of TiO_2	2
7 ml of TiO_2	3
8 ml of TiO_2	4
9 ml of TiO_2	5

When 1 refers to the clearest solution and 5 refers to the most opaque solution.

Figure 4.4 Comparison of different pH with 5 ml of TiO_2 stock solution and 0.3 wt% of PVA

Table 4.3 Degree of transparent with different pH 5 ml of TiO_2 stock solution and 0.3 wt% of PVA

Degree of pH	**Degree of transparent**
pH = 2.0	1
pH = 2.5	1
pH = 3.0	3
pH = 3.5	4
pH = 4.0	5

When 1 refers to the clearest solution and 5 refers to the most opaque solution.

The most stable complex was found with 5 ml of TiO_2 stock solution and 2 ml of glacial acetic acid can be added and keep the solution transparent by adjusting with PVA up to 100 ml. It was showed the clearest solution when observing by necked eyes. The most transparent solution revealed that no unexpected cross-linked formed. The highest quantity of TiO_2 stock solution which can keep the solution transparent was 5 ml, 0.3 wt.% of PVA represented the well-complexes of nanocomposites.

Figure 4.5 Comparison of different concentration of Teflon with 5 ml of TiO_2 stock solution and 0.3 wt% of PVA at pH 2.5

Table 4.4 Degree of transparent with different concentration of Teflon with 5 ml of TiO_2 stock solution and 0.3 wt% of PVA at pH 2.5

Amount of Teflon	Degree of transparent
Teflon 0.60 ml	1
Teflon 0.65 ml	1
Teflon 0.70 ml	1
Teflon 0.75 ml	4
Teflon 0.80 ml	5

When 1 refers to the clearest solution and 5 refers to the most opaque solution.

Teflon was introduced as an additive agent for improving the performance of nanocomposites. It was replaced at every end of long chain PVA. According to the property of Teflon, it will increase lubricity, hydrophobic, and reduce friction. The stable of these nanocomposites can be used in manufacture as friction modifier in lubricant industry in further researches. Teflon cannot be added more than this ratio because of exceeded Teflon will cause free PTFE cross-linking.

Silver have no problem about conglomerate to bigger molecule but its ionic radius which is bigger than Titanium. This makes silver hard to replace in polymer chain. It was added in limited amount. The physical observation showed that suitable quantity of silver nano has yellow or orange color. The brown color of the solution is represented the silver oxide, the more stable complex of silver. This form is hard to reverse to silver nano anymore.

4.2 Characterizations

4.2.1 FT-IR

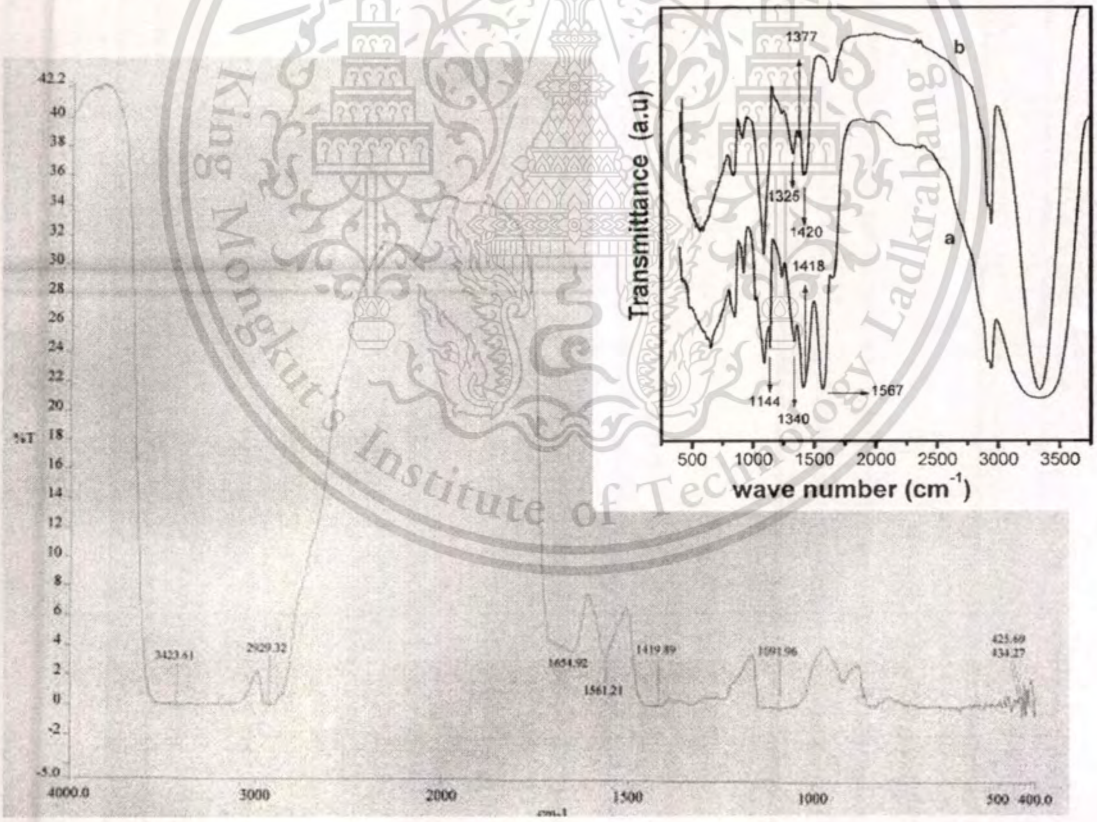


Figure 4.6 FT-IR spectra of the pure PVA compares with principle spectra

Table 4.5 FT-IR Vibration of TiO_2/PVA

Wave Number (cm-1)	Compound
3300-3400	-OH stretching
2800-2950	-CH stretching of alkane
1400-1300	-CH stretching of alkene
1100	-C-O stretching
830	-Ti-O stretching

FT-IR was used to study the main functional groups appeared in different TiO_2/PVA samples prepared from TiO_2 and PVA. For the TiO_2/PVA with the addition of Titanium showed similar pattern to the pure PVA, as expected.

It should be noted that the addition of Titanium into the TiO_2/PVA caused narrow peak in the range of 3500-3300 cm^{-1}, indicating of the change in hydrogen bonds in the TiO_2/PVA samples.

Fig. 4.6 a broad absorption peak is centered on 3320–3340 cm^{-1}, which is due to the presence of hydroxyl group of PVA molecules and adsorbed water. The absorption peaks in the range 2912–2943 cm^{-1} and at 1418 cm^{-1} may correspond to vibration of CH_2 bond in PVA molecules. The comparison of the peak intensities in the range 2912–2943 cm^{-1} and at 1418 cm^{-1} between lines (a) and (b) in Figure 4.6 indicate that the H–C–H group in the PVA molecule keeps the initial state after mixing PVA with TiO_2 sol. The absorption band at 1100 cm^{-1} which is corresponds to stretching motion of bond C–O in the PVA molecule demonstrates high stability of the CC–O group in TiO_2/PVA nanocomposites. The most distinct feature in FT-IR spectra of TiO_2/PVA nanocomposite (Figure 4.6 line (b)) was the disappearance of the absorption band at 1568 cm^{-1}. The interesting phenomenon is the shift of absorption peak in 1340 cm^{-1} region that may correspond to the bending vibration of bond CO–H. In Figure 4.6 line (b) the absorption peak at 1340 cm^{-1} disappears while two new absorption bands appear at 1325 cm^{-1} and 1377 cm^{-1}. The result may be attributed to the formation of a new chemical bond in the TiO_2/PVA nano-composite.

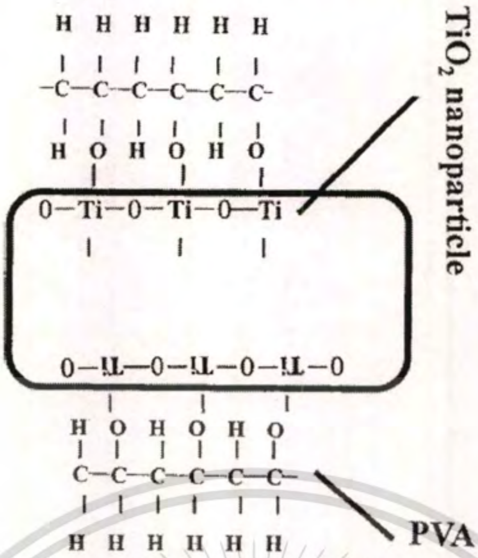


Figure 4.7 Surface structure scheme of the TiO2 particle nano-dispersed in PVA matrixes.

A mechanism of the organic surface modification of the TiO_2 nanoparticles may be obtained as following: It is well known that there are a lot of Ti–OH groups covering the surface region of TiO_2 nanoparticles. When PVA molecules are adsorbed to the surface TiO_2 nanoparticles, Ti–OH groups on the surface of the TiO_2 nanoparticles will react with hydroxyl groups linking to PVA molecules. The dehydration and condensation reaction can occur between the both hydroxyl groups. We can expect that the strong interfacial bond Ti–O–C be formed all over the surface of TiO_2 nanoparticles (see Fig. 4.3). The bond Ti–O–C anchors PVA molecules to the surface of TiO_2 nanoparticles. As a result the surfaces of the TiO_2 nanoparticles were wrapped with a layer of PVA polymer. The stable core-shell microstructure may provide the necessary dispersion function and prevent the agglomeration of TiO_2 nano-particles.

In addition, the peak shift in the range of 3500-3300 cm-1 was also noticed in the PVA-TiO_2 reinforced by different contents and physical appearance of solution, suggesting the range in intermolecular hydrogen bonding of nanocomposites.

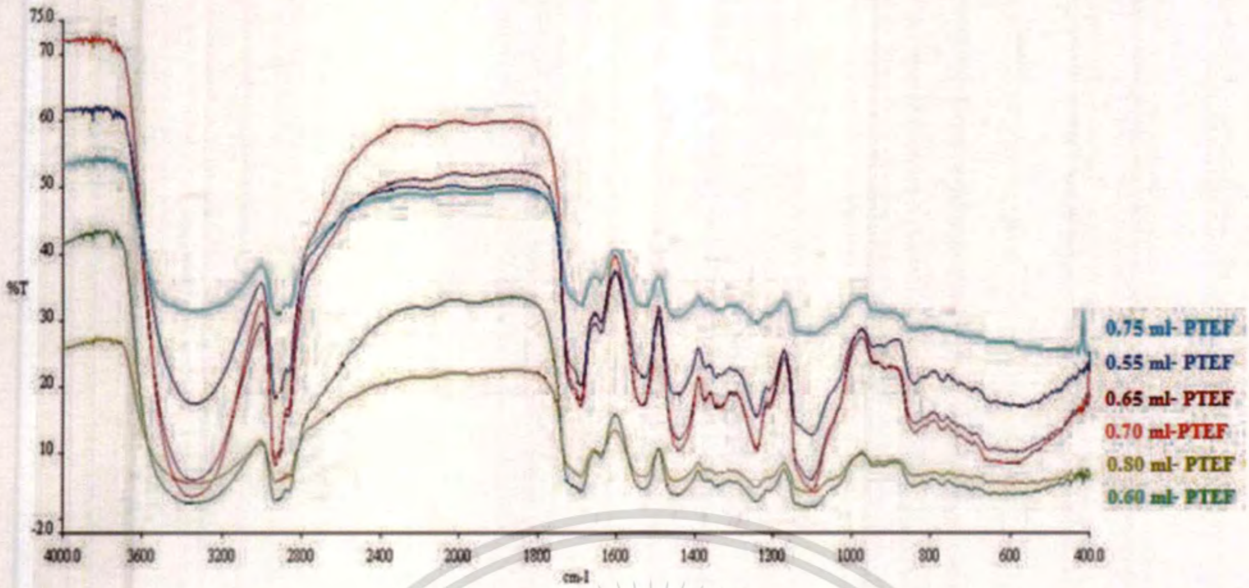


Figure 4.8 FT-IR spectra of the TiO_2/PVA with different amounts of Teflon

Table 4.6 FT-IR Vibration of TiO_2/PVA-PTFE

Wave Number (cm-1)	Compound
3600-3700	Ti-OH stretching
3300-3400	OH stretching
1440	OH bending
2800-2950	CH stretching of alkane
1400-1300	CH stretching of alkene
1690-1800	C=O stretching
1100 and 1240	C-F of Teflon
830	Ti-O stretching

Figure 4.8 shows IR spectra of TiO_2/PVA plasticized by Teflon. It was found that similar IR spectra were obtained for the TiO_2/PVA prepared from various quantity of Teflon. Comparison with IR spectra of the PVA/TiO_2 in the range of 3700-3600 cm^{-1}, 3400-3300 cm^{-1}, and 1340 cm^{-1}, related to Ti-OH stretching, OH

stretching, and OH bending, respectively. The range of 2943–2912 cm^{-1} with 1420-1330 cm^{-1}, and 1600-1700 cm^{-1} are referred to CH stretching and CO stretching. The appearance of the absorption band at 1240 cm^{-1} and 1100 cm^{-1} are referred to C-F stretching of Teflon (PTFE). The absorption peaks in 730 cm^{-1} region are corresponding to the stretching vibration of bond Ti-O. The difference was found in FT-IR absorbance graph, i.e. 3320 cm^{-1} shifted to 3340 cm^{-1} for PVA, and 1100 cm^{-1} shifted to 1110 cm^{-1} for Teflon. The results of peak position shifts indicated the increasing of molecular hydrogen bonding by the addition of Teflon.

Results of Fourier transform infrared spectroscopy for TiO_2/PVA and Ag-TiO_2/PVA-PTFE composites films calcined are shown in Figure 4.9 The spectra show several peaks observed such as 3433, 1643 and 478 cm^{-1}. The spectra at 3413 and 1626 cm^{-1} are -OH stretching of TiO_2 surfaces (Ti-OH) and O-H bond of hydroxyl group, respectively. The 535 cm^{-1} spectrum is Ti-O bond.

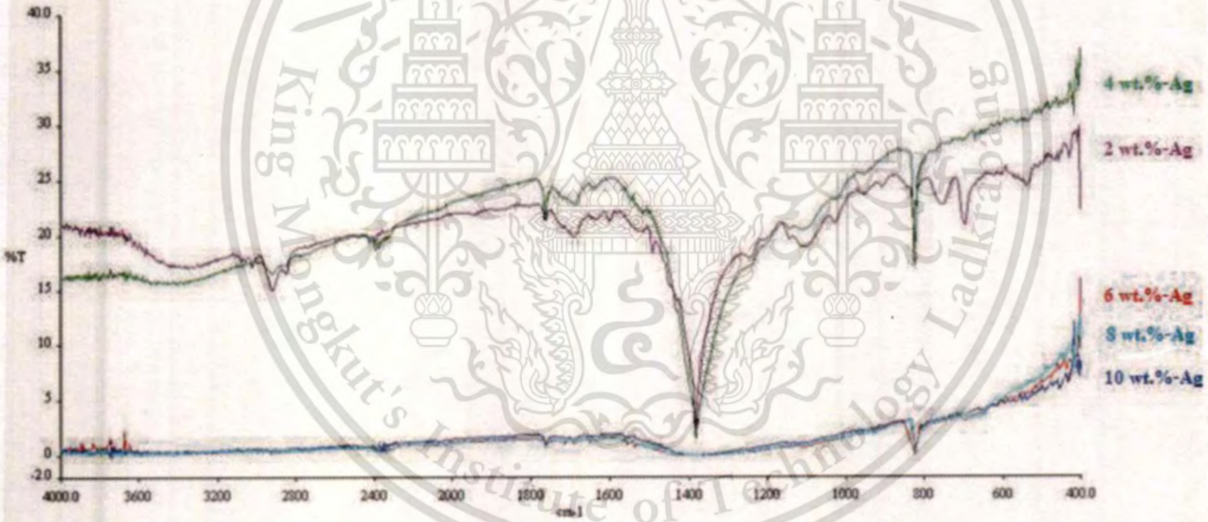


Figure 4.9 FT-IR spectra of TiO_2/PVA -PTFE with different amounts of Silver

Table 4.7 FT-IR Vibration of Ag-TiO_2/PVA-PTFE

Wave Number (cm-1)	Compound
3600-4000	Ti-OH stretching
2800-2950	CH stretching of alkane
2300	N=C=O stretch
1690-1800	C=O stretching
1385	NO_3 stretching
830	Ti-O stretching
570	Ag-O stretching
419	Ag-N stretching

Figure4.9 shows IR spectra of TiO_2/PVA -PTFE plasticized by Silver. It was found that similar IR spectra were obtained for the TiO_2/PVA prepared from various quantity of Silver. Comparison with IR spectra of the TiO_2/PVA doped with silver in the range of 4000-3600 cm^{-1}, 3000-2900 cm^{-1}, and 1385 cm^{-1} related to Ti-OH stretching, CH stretching, NO_3^- stretching, respectively.

The appearances of the absorption band at 419 cm^{-1} are referred to Ag-N stretching. The absorption peaks in 824 cm^{-1} region are corresponding to the stretching vibration of metal-OH bond, Ag-OH. The difference was found in FT-IR absorbance graph such as slightly shifted. The results of peak position shifts indicated the increasing of molecular hydrogen bonding by the addition of Silver.

4.2.2 UV-Visible spectrometer

The percentage of transmittance of UV (800-190 nm) and visible light (400-60 nm) of TiO_2/PVA with Teflon were measured. Figure 4.10 shows the UV-visible spectra of Pure PVA and TiO_2/PVA nanocomposites.

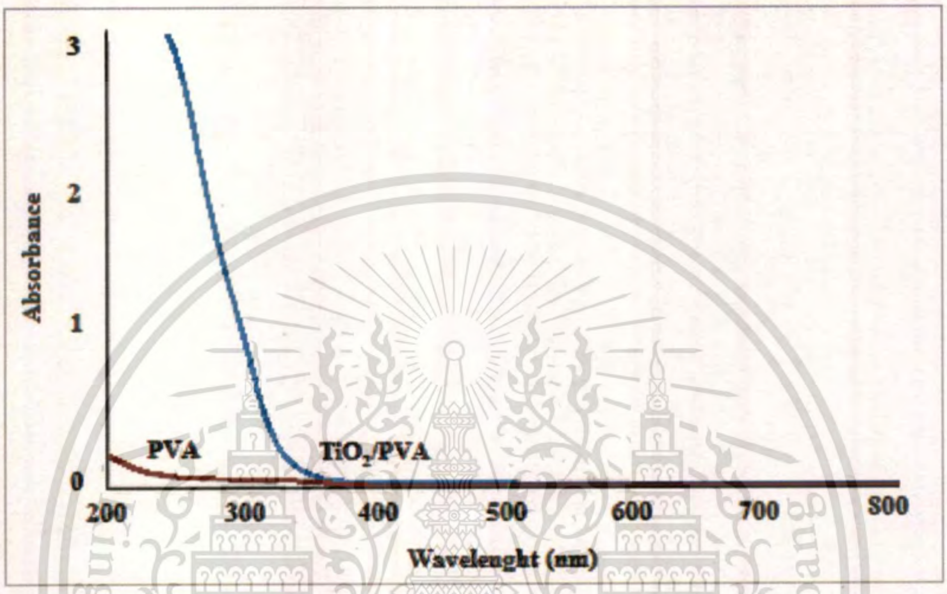


Figure 4.10 UV spectra of Pure PVA compares with principle spectras

UV-Vis absorption spectra of Fig. 4.7 taken from the TiO_2/PVA nanocomposites sol solution displays intense absorption of UV radiation. With the increased TiO_2 content the UV radiation absorption edge moved to the longer UV wavelength region. Visible light can transmit through the TiO2/PVA nanocomposite sol solution. The good transparency for visible light is a particular feature of the inorganic/polymer nano-composite in which the aggregation of nano-particles was successfully inhibited.

From 4.11, it was seen that the percentage of transmittance decrease when the amount of Titanium with Teflon was increased. As if, the absorbance of these nanocomposites was focused, it was found that their absorbance was higher in UV range, especially UV-A and UV-B.

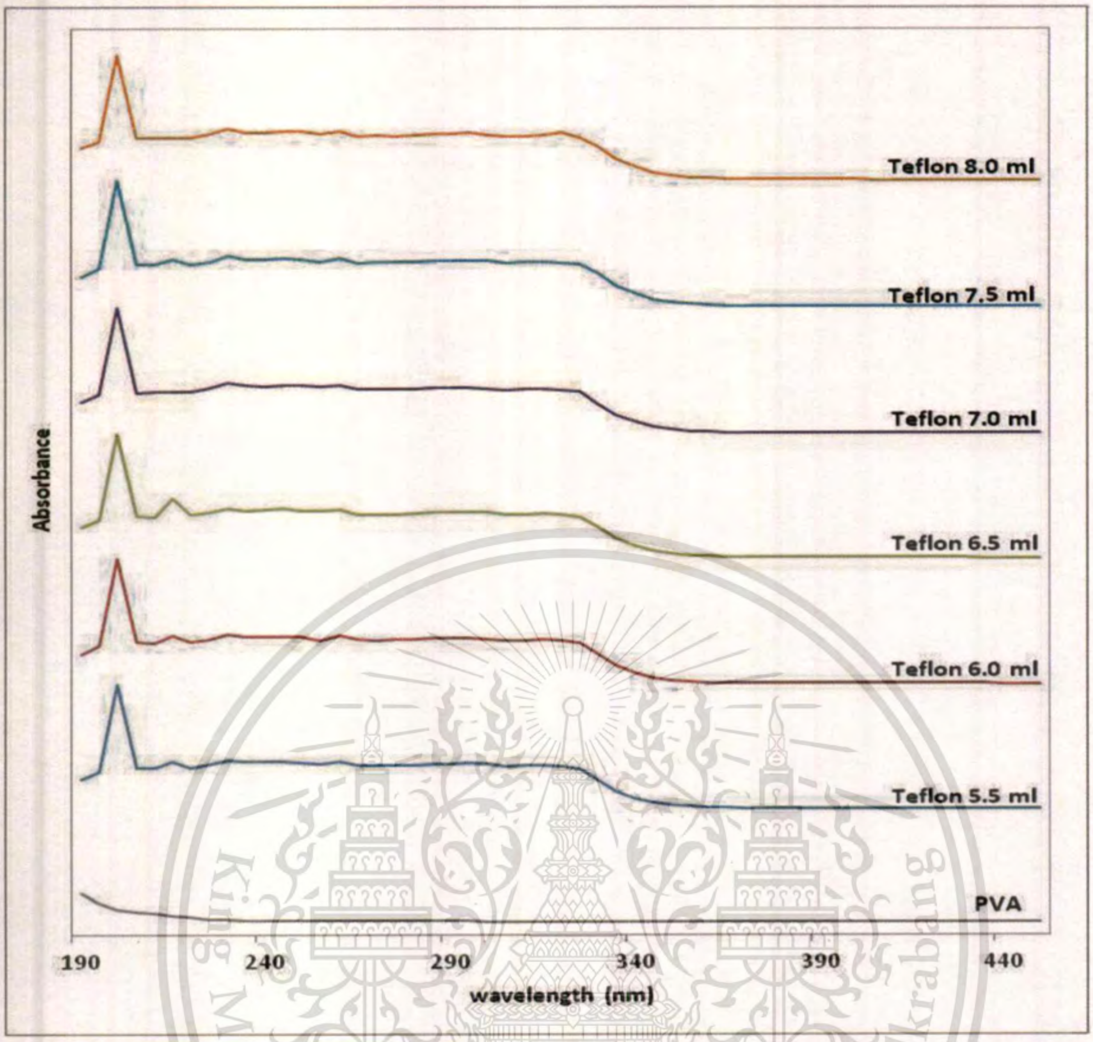


Figure 4.11 UV-visible spectra of PVA and TiO_2/PVA-PTFE containing in various amounts

The UV-visible diffuse reflectance spectra of the samples are shown in Figure 4.11. It can be seen that all samples were strong absorptions in the ultraviolet region. The absorption edge of Ag-TiO2 composites moved to longer wavelength in comparison with pure TiO_2 indicating the band gap was decreased by doping with Ag. The calculated band gap energy of pure TiO_2 and Ag-TiO_2 are 2.98 and 2.74 respectively. The photocatalytic reaction over P. Aeruginosa disinfection of Ag-TiO_2 should be high activity due to the electron–hole pair separation efficiency induced by enhancing the charge pair separation and inhibiting their recombination by the Ag dopant.

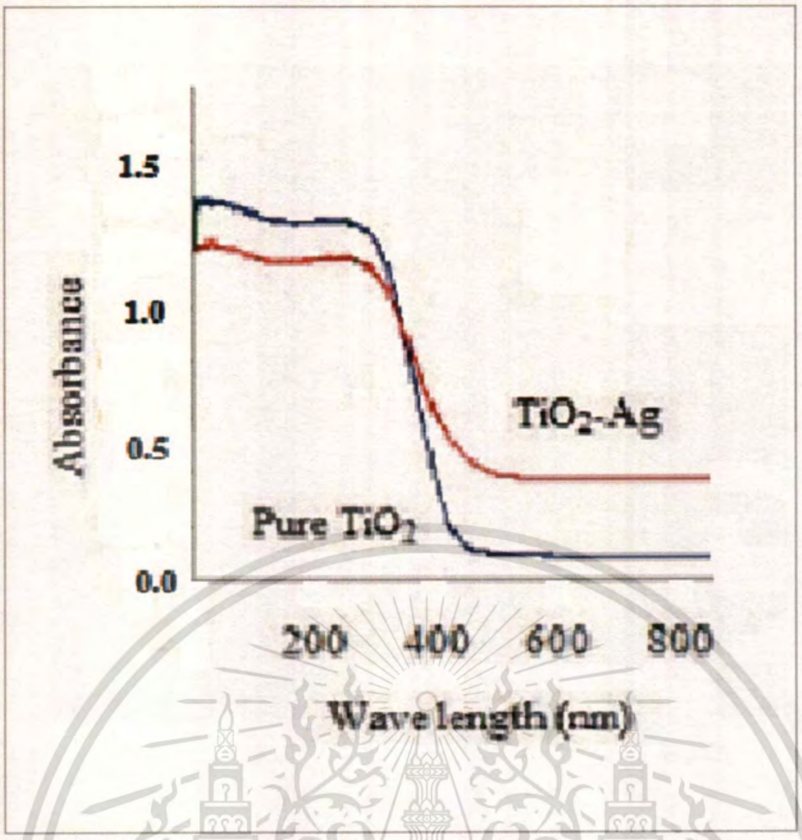


Figure 4.12 An example of UV-Vis spectra of pure TiO_2 and Ag-TiO_2 sol solution

The peak at 200-240 nm is appropriated for carbonyl groups conjugated with one, in line, ethylenic group. The weak shoulder at 344 nm is attributed to –C(CH=CH)$_3$CO- structure. No broad peak appears at 443 nm for all of $AgNO_3$ filled the PVA. This band is characteristic of chelate formation for Ag^+ coordinated with the hydroxyl group of PVA.

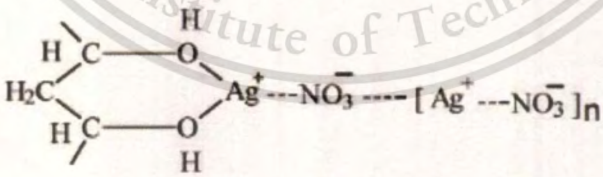
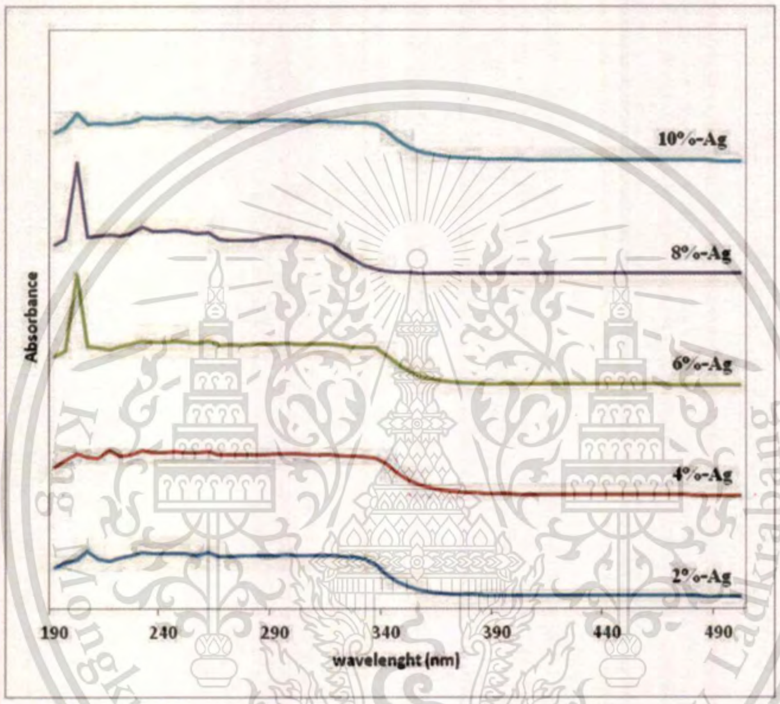
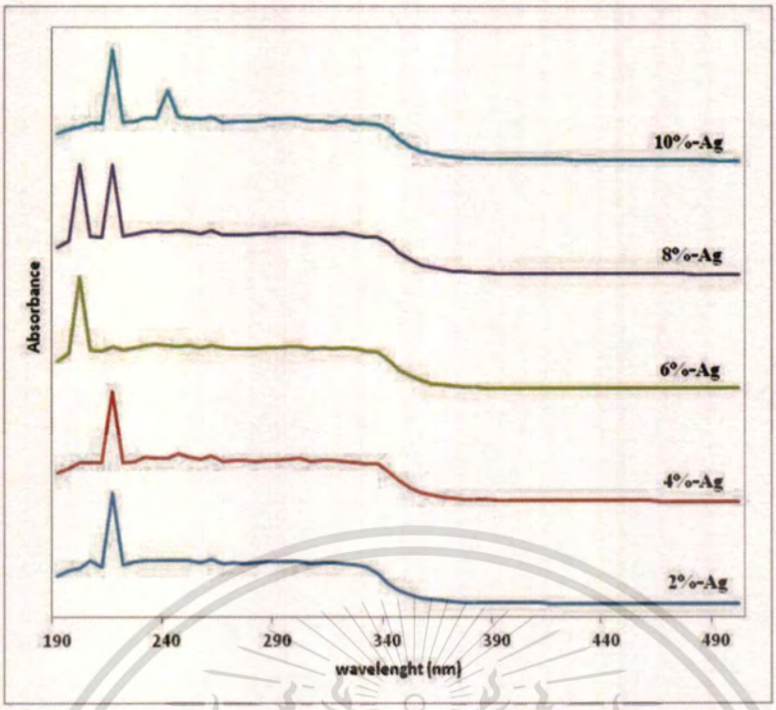


Figure 4.13 Structure of Ag^+/PVA

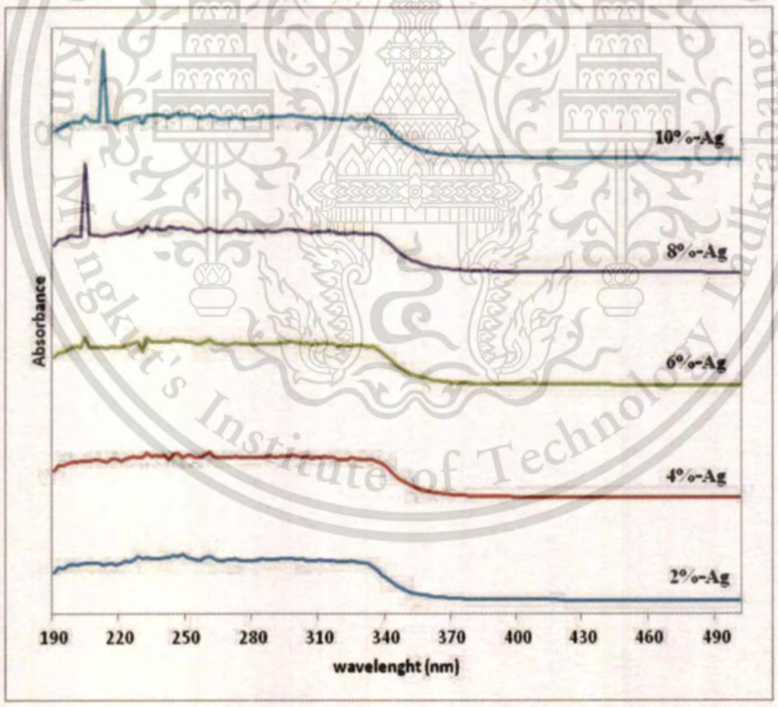
UV-vis absorption spectra of Figure 4.14 taken from the TiO_2/PVA-PTEF nanocomposites sol solutions display intense absorption of UV radiation. With the increased Ag content the free Titanium ion absorption peak is increased the absorbance. The comparison between the first day and the fifth day of the solution shows that the UV radiation absorption edge slightly moved to the longer UV wavelength region. Visible light can transmit through the nanocomposites sol solutions. The shifted from 200 to 240 nm is corresponding to TiO_2/PVA bond as the FT-IR graph



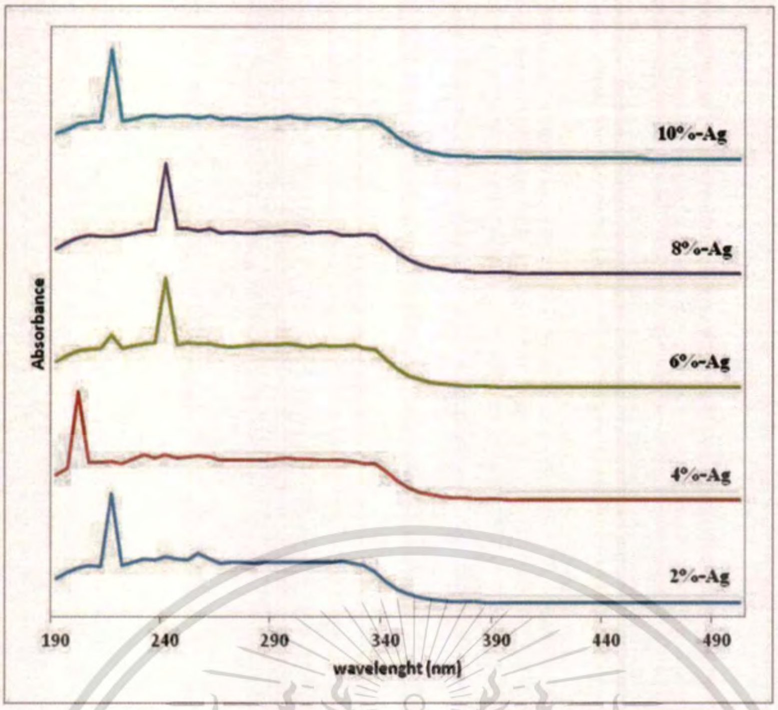
(a)


10%-Ag
8%-Ag
6%-Ag
4%-Ag
2%-Ag
Absorbance
190
240
290
340
390
440
490
wavelenght (nm)

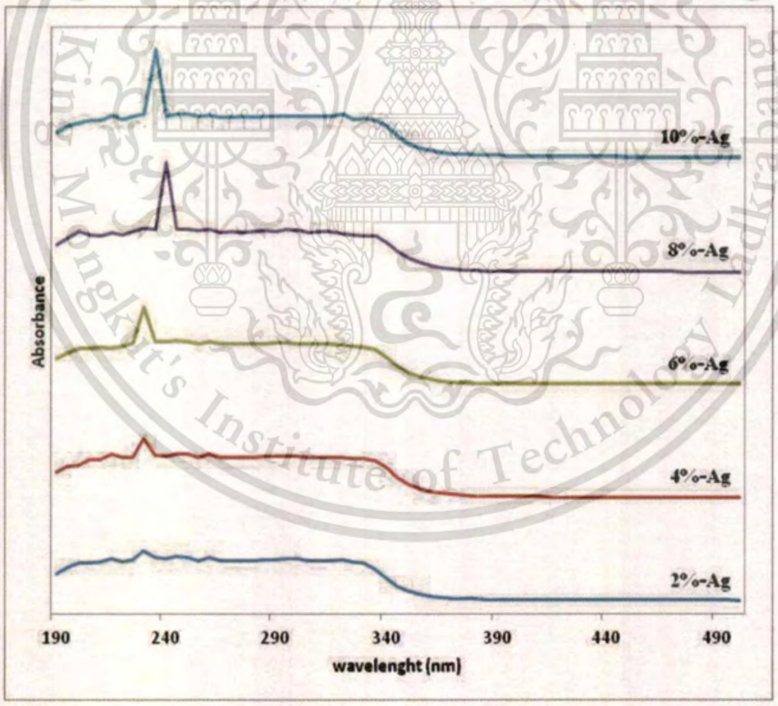
(b)


10%-Ag
8%-Ag
6%-Ag
4%-Ag
2%-Ag
Absorbance
190
220
250
280
310
340
370
400
430
460
490
wavelenght (nm)

(c)



(d)



(e)

Figure 4.14 The UV-Vis spectras of TiO_2/PVA-PTEF in various amounts (a) Day 1st, (b) Day 2nd, (c) Day 3rd, (d) Day 4th, and (e) Day 5th.

Chapter 5

Conclusion and Suggestions

5.1 Conclusion

In this work, TiO_2/PVA nanocomposites were prepared by sol-gel method. It was found that PTFE or Teflon affects to lubricity, hydrophobic, and friction of nanocomposite. The photocatalytic activity of the nanocomposites is obviously improved due to the synergistic effect of three components. Structures of nanocoposites were studied by FT-IR and UV-Vis spectrometry. The Teflon doped in nanocomposites resulted in an excellent bonding. Compared to bare PVA and TiO_2/PVA shows much higher activity visible light and UV region. The reason for this enhancement is that the metal ion acted as an electron acceptor, the influence of which strongly depended on the kind of metal ion. The highest quantity ratio of Titanium and Teflon that can be added and adjust volume with PVA to 100 ml is 5 ml : 0.7 ml / 0.3wt.% of PVA at pH 2.5 was found. According to the agglomeration of short chains and crosslinking, Teflon and Titanium can be added in a limited amount.

Silver cannot replace in the position of Titanium in the TiO_2/PVA nanocomposites because bonding of Ag/PVA is not stable or not strong enough to stabilize the compound. PVA can be modified by adding PVP or W (tungsten). Functional group of PVA has π bonding with OH functional group will increase the formation of bond between Ag and PVA. Ag-TiO_2 bond is corresponding to photocatalyst, kill bacteria directly. Band gap of Ag and Ti are nearly in UV and Visible light region. When UV beam pass through, it will generate high energy of electron at conduction band. Electrons excite from valence band to conduction band. High energy potential hole at valence band is occurred as well. This accelerates photocatalytic reaction under UV and Visible-light irradiation. A well-crystallized support could reduce the charge recombination thus enhance the lifetime of charge carriers and the better performance is expected.

If silver can be replaced at the position of Titanium in TiO_2/PVA nanocomposite, the transmittance of UV-Vis spectra will appear at 360-420 nm. There are no spectra at that position. It is corresponding to IR results which show the absorbance peak of -OH stretching of water at 1635 cm^{-1}

with metal bonding, Ag. There is some drawback of silver that should overcome soon. Cumulative of silver in nature may destroy some salutary bacteria. This will cause an unbalancing environment. Silver has bigger radius than Titanium. It is hard to replace in that position. A low stability of silver makes it hydrolyze by H_2 to be AgO at room temperature.

5.2 Suggestions

There are some polymers that might be more appropriate with Ag than PVA which is lower basic property for example PVP. It can be added to improve the activity of replacing with Ag. Ag-Ti/PVA-Teflon was not suitable to form a film or coating material, spinning method might be more preferable for this sol solution. Longer time may be needed for perfectly bonding between metal and matrix.

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Appendices

Appendix A

Physical Properties

A.1 Titanium isopropoxide

Table A.1 Physical properties of Titanium isopropoxide

Properties	
Molecular formula	$C_{12}H_{28}O_4Ti$
Molar mass	284.215 g/mol
Appearance	colorless to light-yellow liquid
Density	0.96 g/cm^3
Melting point	17 °C, 290 K, 63 °F (approx.)
Boiling point	232 °C, 505 K, 450 °F
Solubility in water	Reacts to form TiO_2
Solubility	soluble in ethanol, ether, benzene, chloroform
Refractive index (n_D)	1.46

A.2 Titanium dioxide

Table A.2 Physical properties of Titanium dioxide

Properties	
Molecular formula	TiO_2
Molar mass	79.866 g/mol
Appearance	White solid
Odor	odorless
Density	4.23 g/cm^3
Melting point	1843 °C
Boiling point	2972 °C
Solubility in water	insoluble
Refractive index (n_D)	2.488 (anatase) 2.583 (brookite) 2.609 (rutile)

A.3 Ethanol

Table A.3 Physical properties of Ethanol

Properties	
Molecular formula	C_2H_6O
Molar mass	46.07 g mol^{-1}
Appearance	Colorless liquid
Density	0.789 g/cm^3
Melting point	−114 °C, 159 K, -173 °F
Boiling point	78.37 °C, 352 K, 173 °F
log P	-0.18
Vapor pressure	5.95 kPa (at 20 °C)
Acidity (pK_a)	15.9[2]
Basicity (pK_b)	-1.9
Refractive index (n_D)	1.36
Viscosity	0.0012 Pa s (at 20 °C)
Dipole moment	1.69 D

A.4 Polyvinyl alcohol

Table A.4 Physical properties of Polyvinyl alcohol

Properties	
Molecular formula	$(C_2H_4O)_x$
Density	1.19-1.31 $g{\cdot}cm^{-3}$
Melting point	220-240 °C
Boiling point	230-250 °C

A.5 Acetic acid

Table A.5 Physical properties of Acetic acid

Properties	
Molecular formula	$C_2H_4O_2$
Molar mass	60.05 g mol^{-1}
Appearance	Colourless liquid
Density	1.049 g cm^{-3}
Melting poi	16-17 °C, 289-290 K, 61-62 °F
Boiling point	118-119 °C, 391-392 K, 244-246 °F
Solubility in water	Miscible
log P	-0.322
Acidity (pK_a)	4.792
Basicity (pK_b)	9.198
Viscosity	1.22 mPa s
Dipole moment	1.74 D

A.6 Silver nitrate

Table A.6 Physical properties of Silver nitrate

Properties	
Molecular formula	$AgNO_3$
Molar mass	169.87 g mol^{-1}
Appearance	white solid
Density	4.35 g/cm^3
Melting point	212 °C, 485 K, 414 °F
Boiling point	444 °C, 717 K, 831 °F (*decomp.*)
Solubility in water	1.22 kg/L (0 °C) 2.16 kg/L (20 °C) 4.40 kg/L (60 °C) 7.33 kg/L (100 °C)
Solubility	soluble in ethanol and acetone

A.7 Polytetrafluoroethylene

Table A.7 Physical properties of Polytetrafluoroethylene

Properties	
Molecular formula	$(C_2F_4)_n$
Density	2200 kg/m^3
Melting point	327 °C
Thermal expansion	$135 \cdot 10^{-6}$ K^{-1} [10]
Thermal diffusivity	0.124 mm²/s [11]
Young's modulus	0.5 GPa
Yield strength	23 MPa
Bulk resistivity	10^{18} Ω·cm [12]
Coefficient of friction	0.05–0.10
Dielectric constant	ε=2.1,tan(δ)<5(-4)
Dielectric constant (60 Hz)	ε=2.1,tan(δ)<2(-4)
Dielectric strength (1 MHz)	60 MV/m

Appendix B

Experimental Data

B.1 FT-IR Data

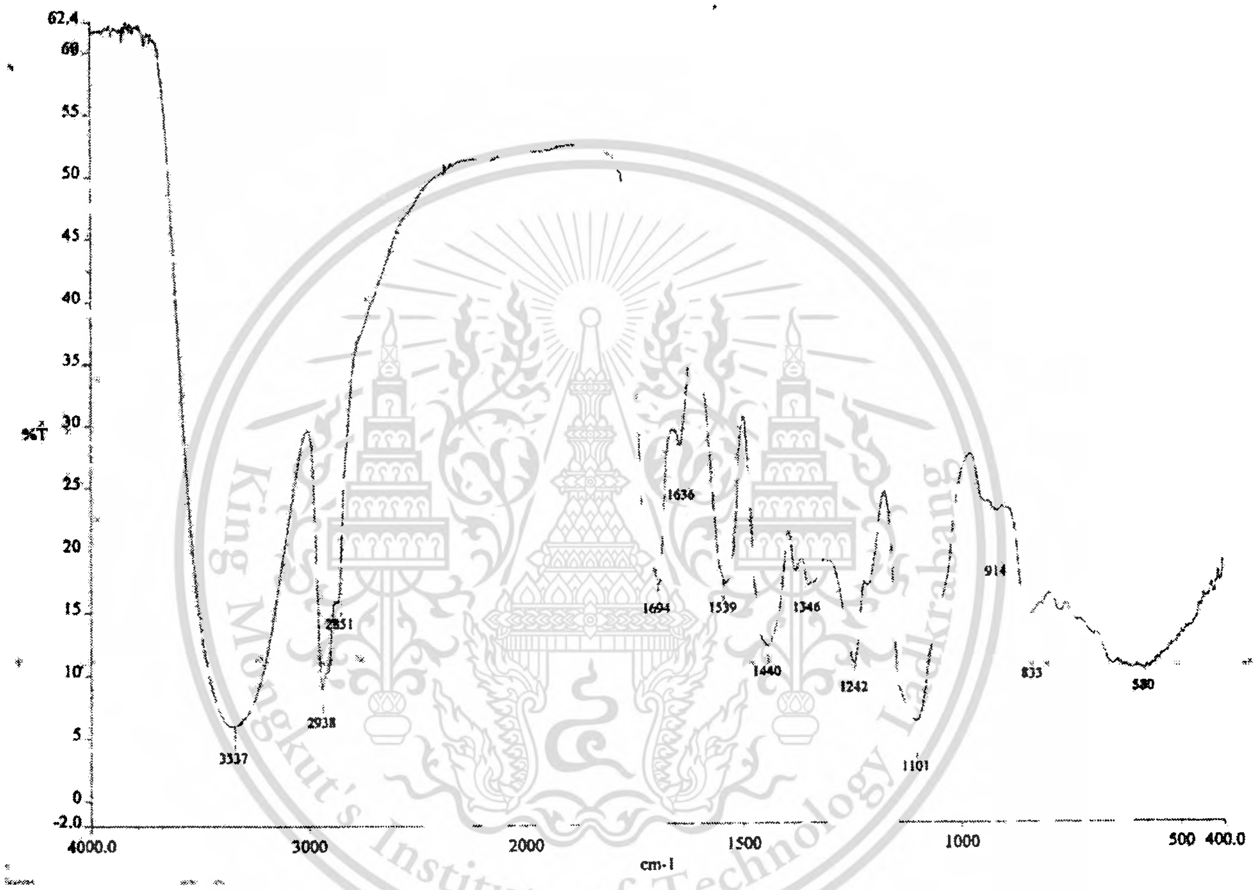

Figure B.1.1 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.55 ml Teflon

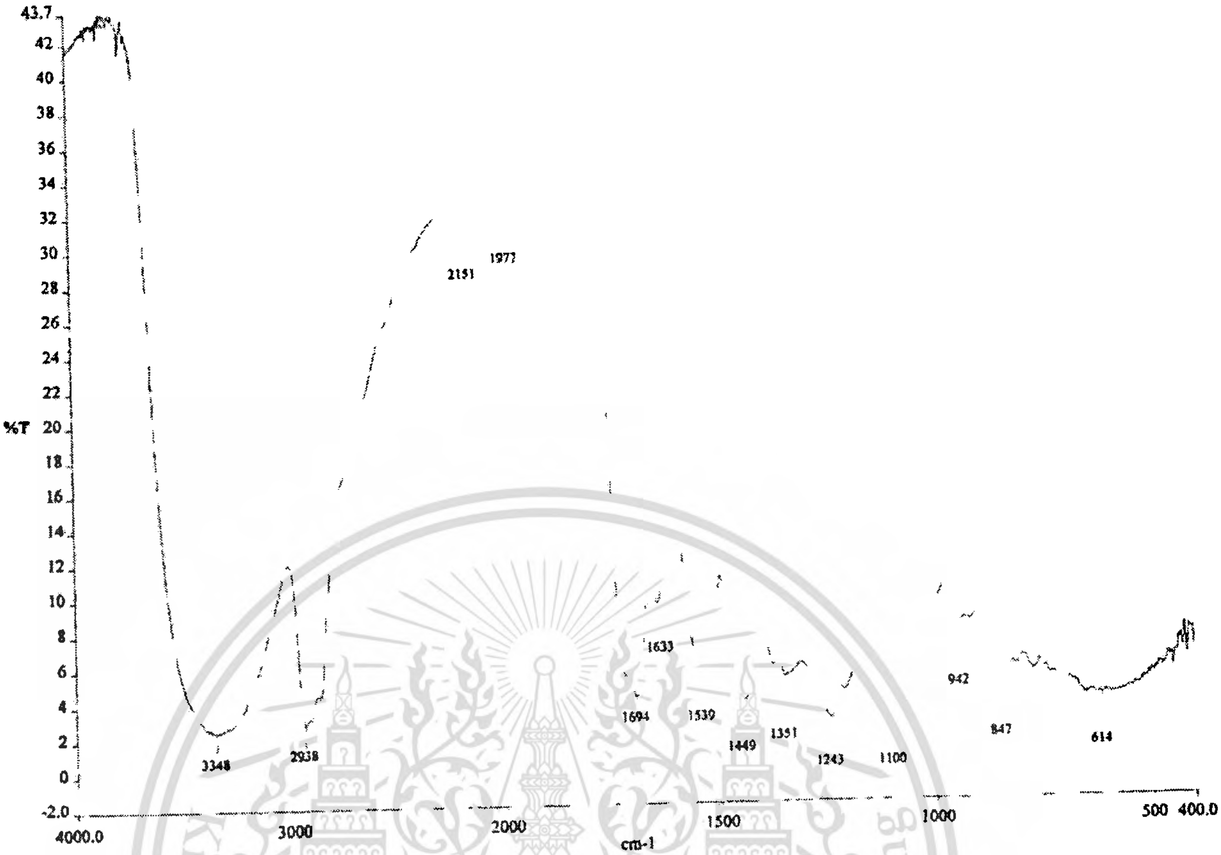

Figure B.1.2 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.60 ml Teflon

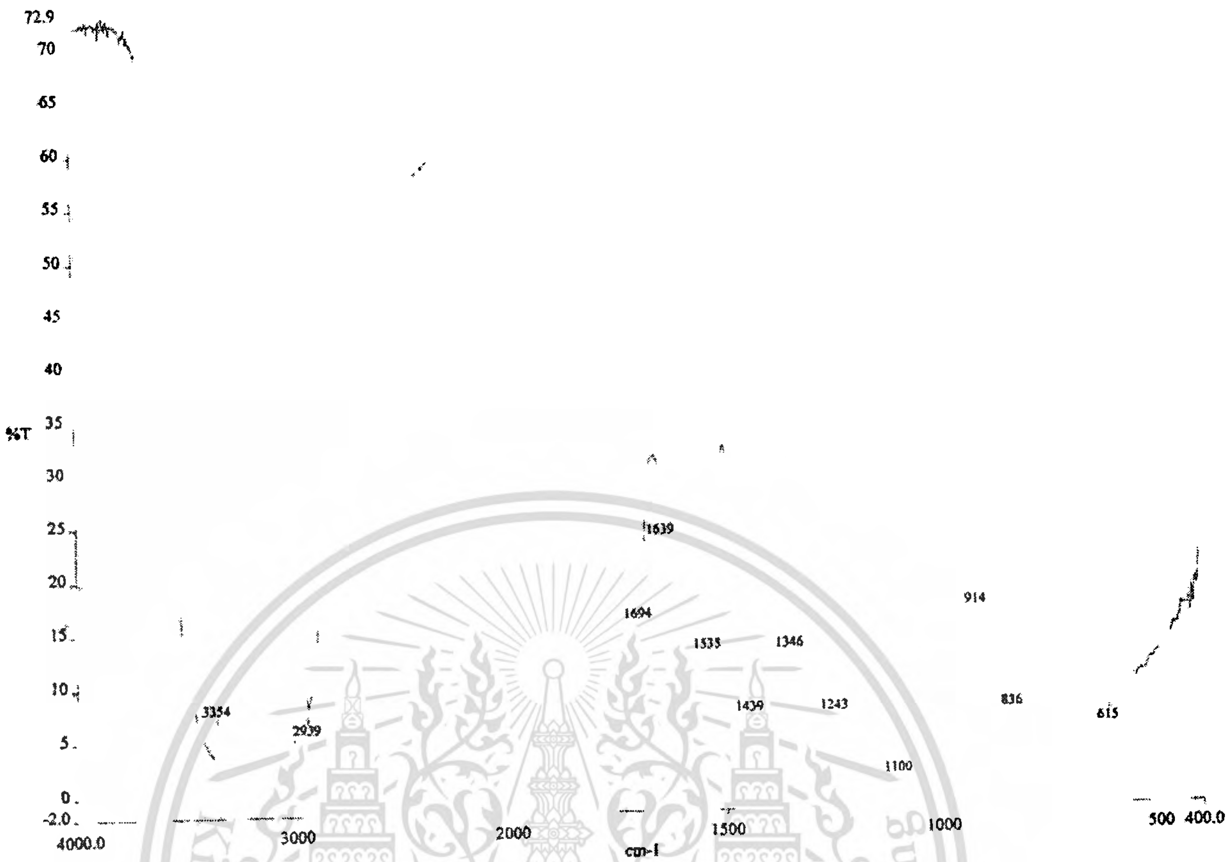

Figure B.1.3 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.65 ml Teflon

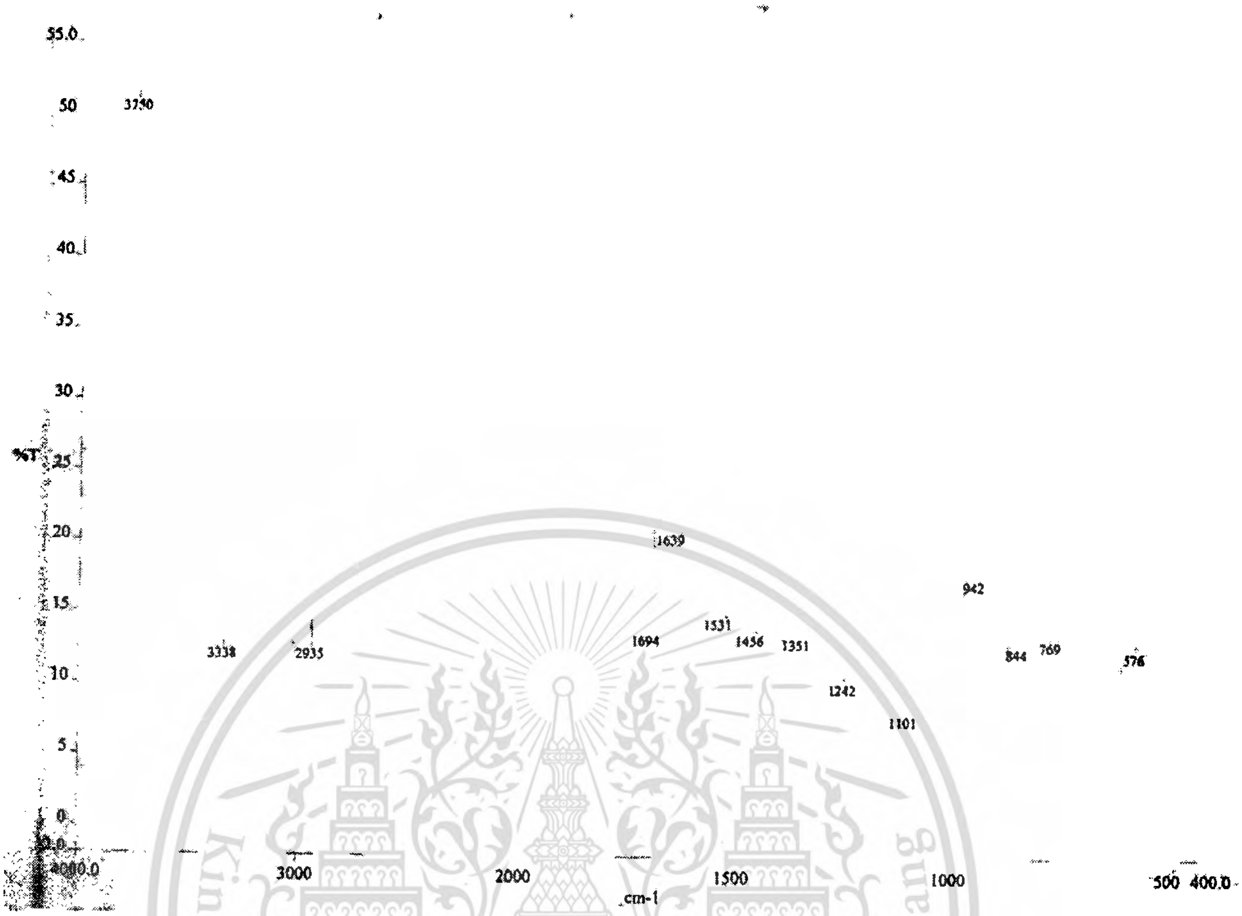

Figure B.1.4 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.70 ml Teflon

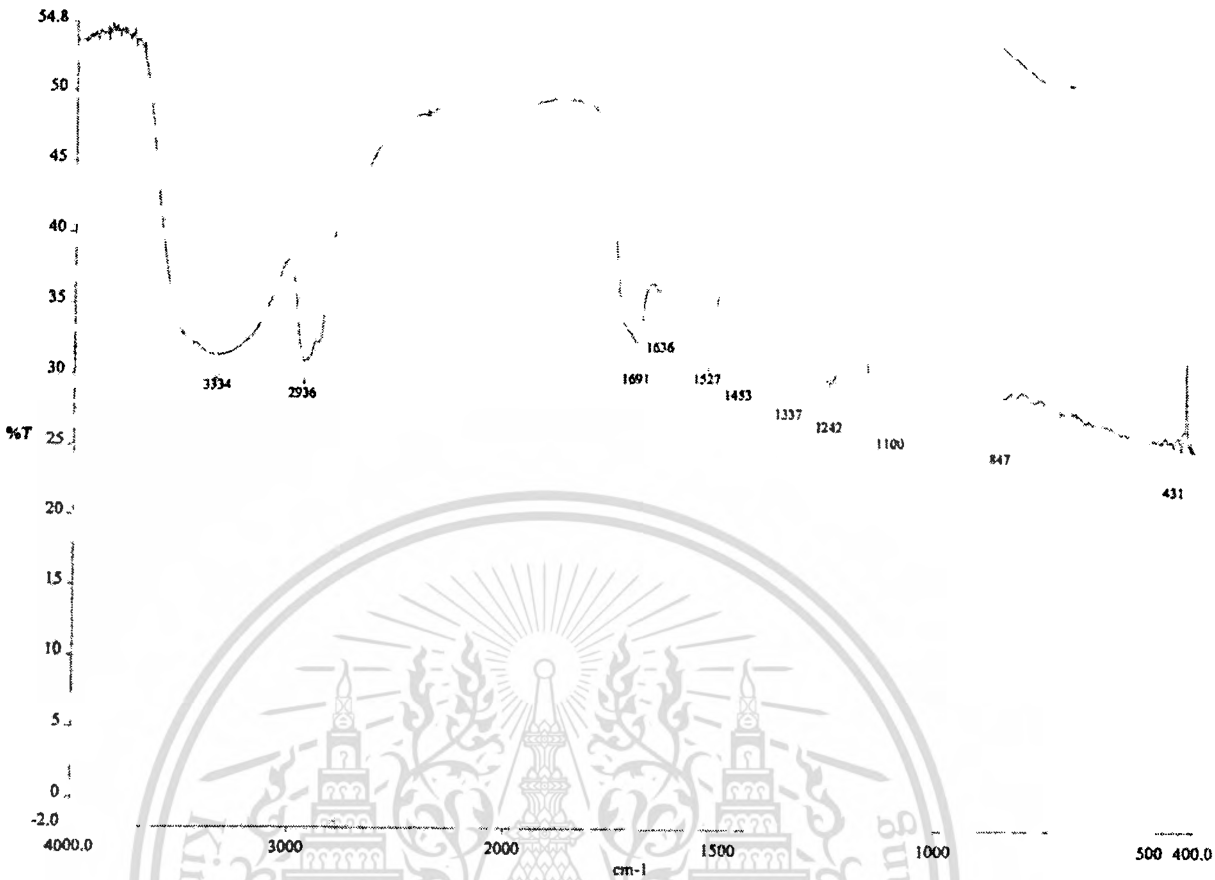

Figure B.1.5 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.75 ml Teflon

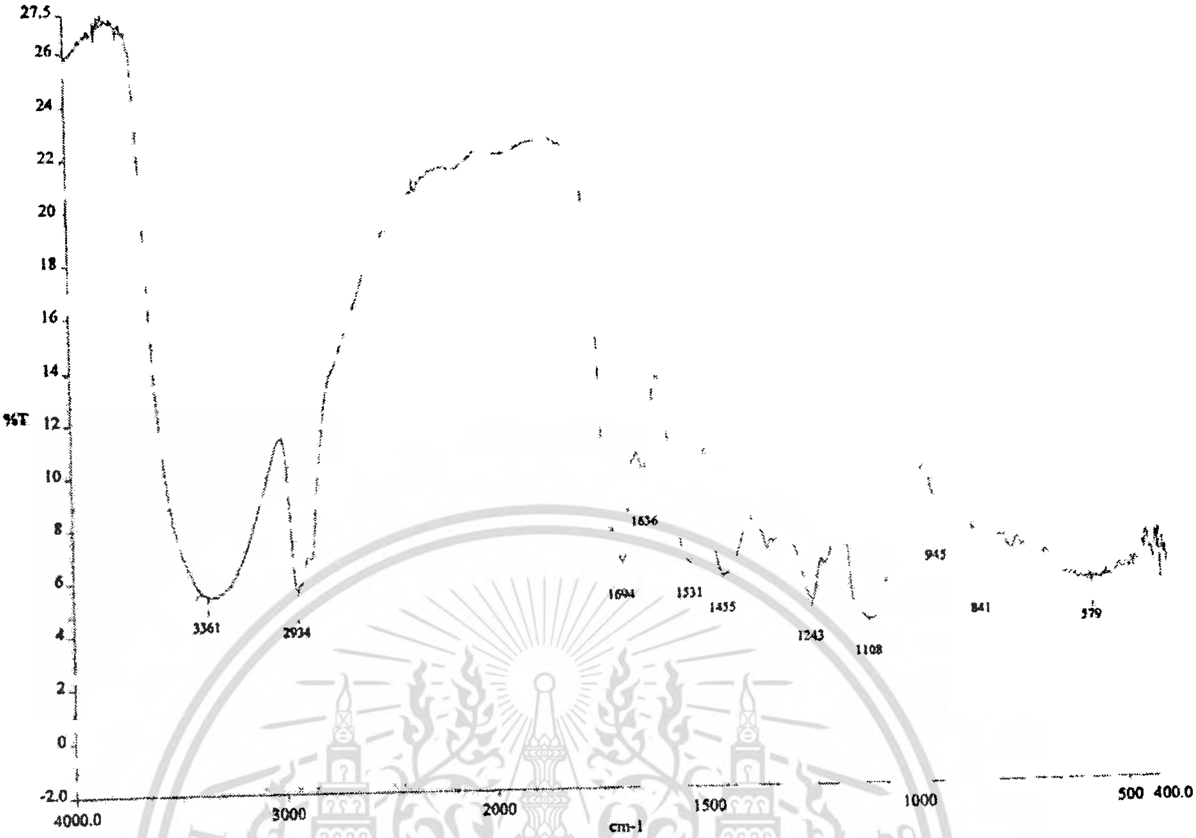

Figure B.1.6 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.80 ml Teflon

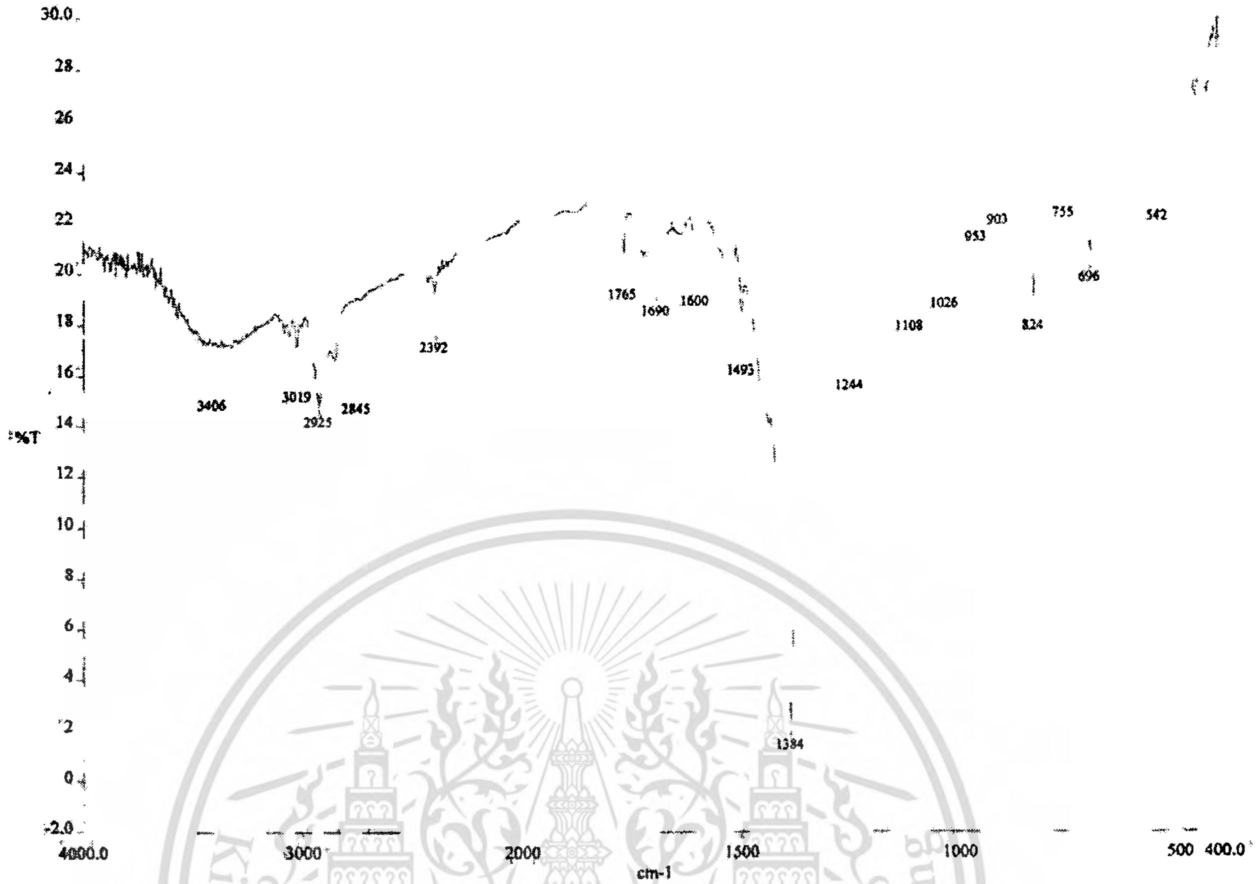

Figure B.1.7 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.7 ml Teflon : 2 wt.% Ag

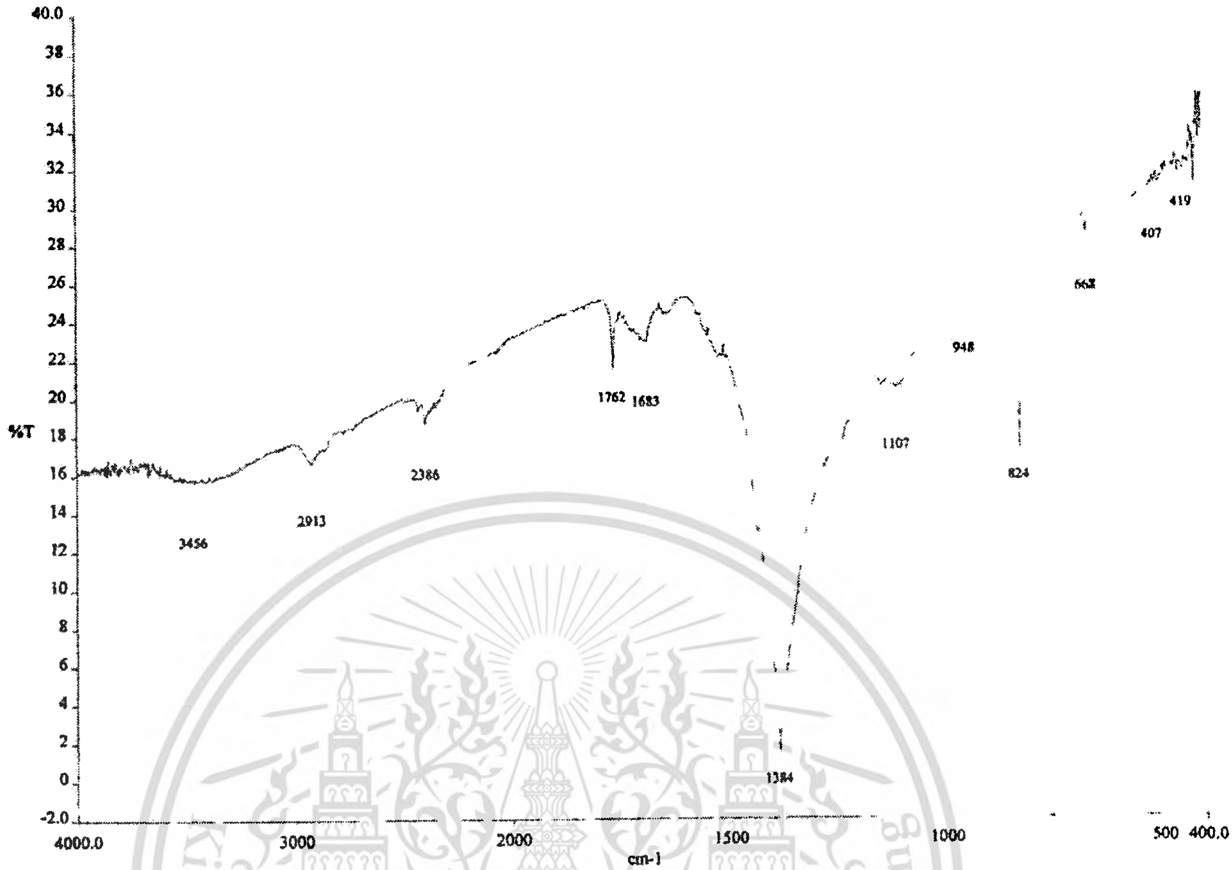

Figure B.1.8 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.7 ml Teflon : 4 wt.% Ag

Figure B.1.9 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.7 ml Teflon : 6 wt.% Ag

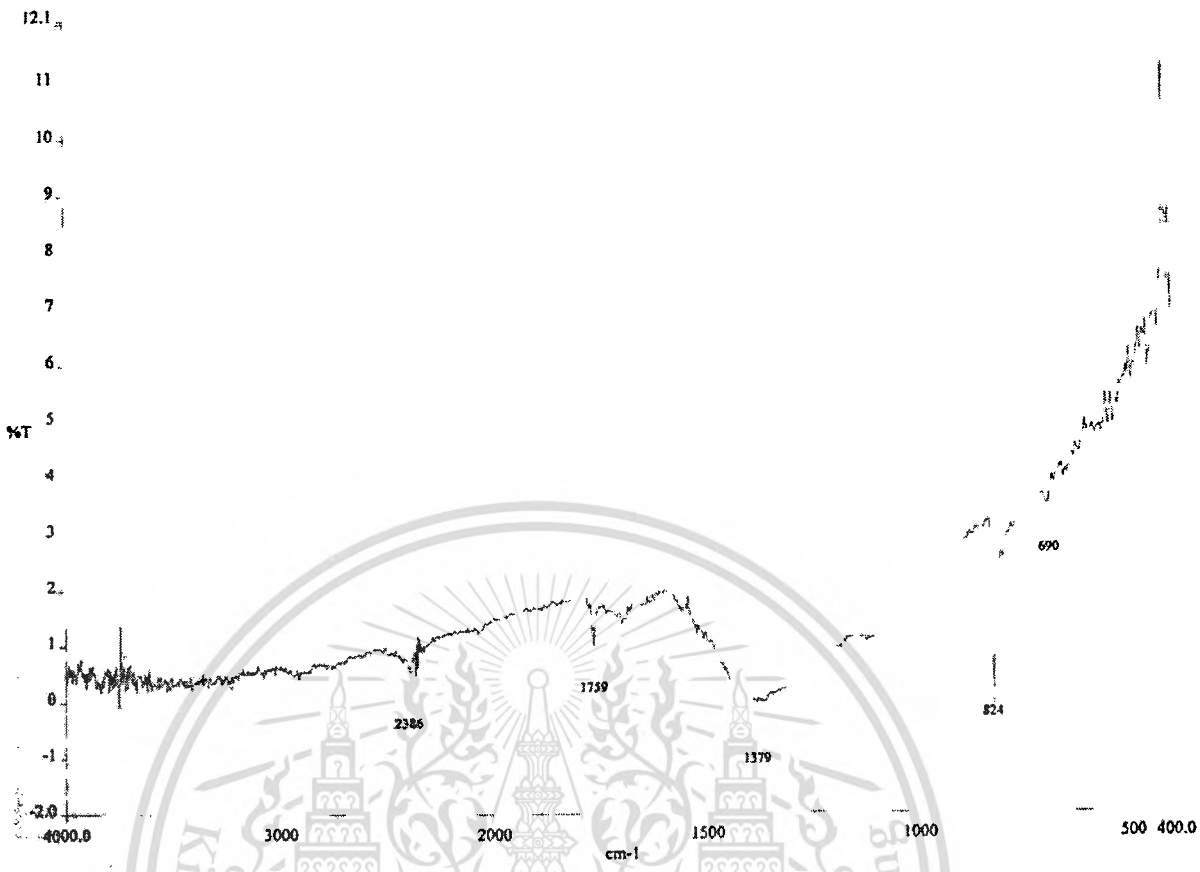

Figure B.1.10 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.7 ml Teflon : 8 wt.% Ag

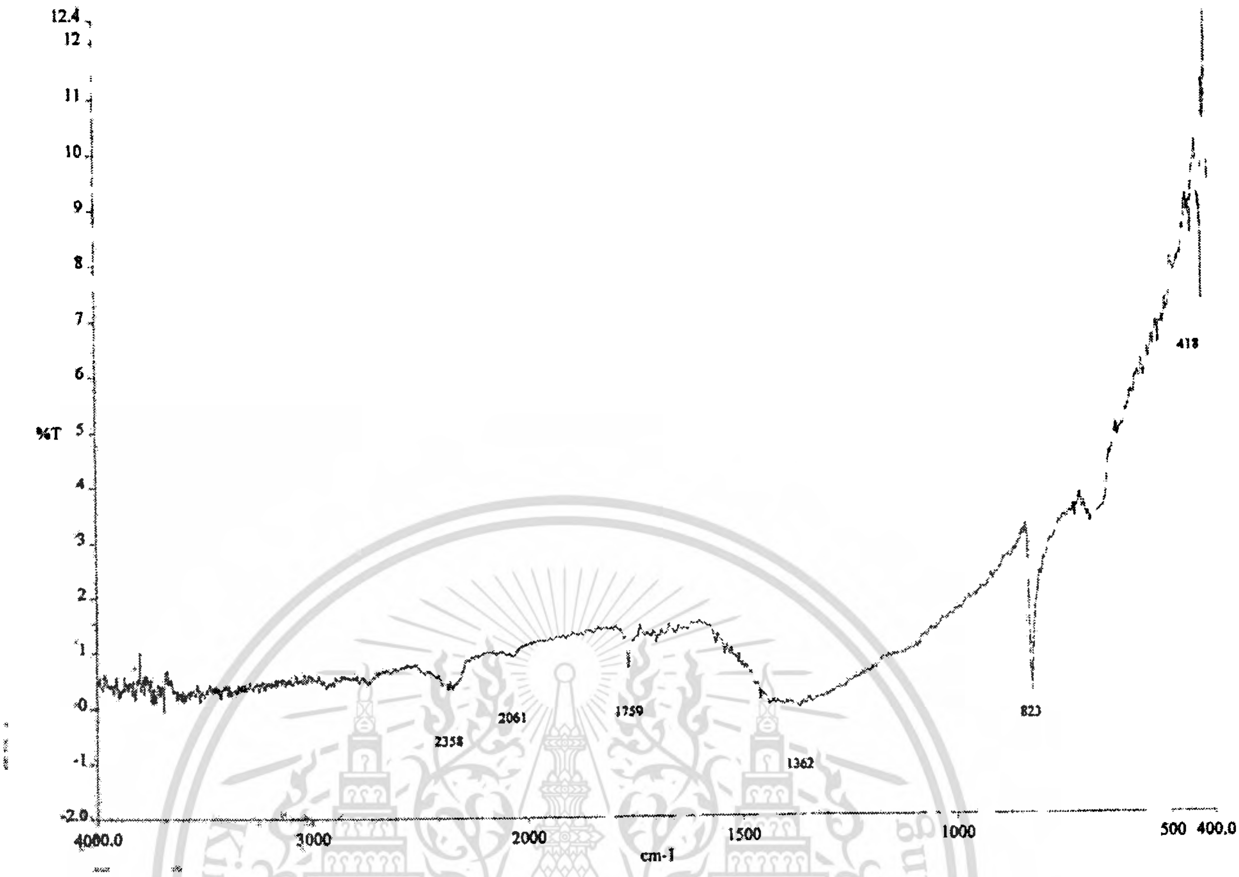

Figure B.1.11 The structure of 0.3 wt.% of PVA : 5 ml Ti solution : 0.7 ml Teflon : 10 wt.% Ag

B.2 UV-Vis spectra

Figure B.2.1 The UV-Vis absorbance of PVA solution

Appendix C

Observation of solution

Figure C.1 The Observation of 5 ml of TiO_2 stock solution : 0.7 ml of Teflon mixed with 0.3 wt.% of PVA solution and various amount of $AgNO_3$ (2, 4, 6, 8 and 10 g), 1st day

Figure C.2 The Observation of 5 ml of TiO_2 stock solution : 0.7 ml of Teflon mixed with 0.3 wt.% of PVA solution and various amount of $AgNO_3$ (2, 4, 6, 8 and 10 g), 2nd day

Figure C.3 The Observation of 5 ml of TiO_2 stock solution : 0.7 ml of Teflon mixed with 0.3 wt.% of PVA solution and various amount of $AgNO_3$ (2, 4, 6, 8 and 10 g), 3[rd] day

Figure C.4 The Observation of 5 ml of TiO_2 stock solution : 0.7 ml of Teflon mixed with 0.3 wt.% of PVA solution and various amount of $AgNO_3$ (2, 4, 6, 8 and 10 g), 4^{th} day

Figure C.5 The Observation of 5 ml of TiO_2 stock solution : 0.7 ml of Teflon mixed with 0.3 wt.% of PVA solution and various amount of $AgNO_3$ (2, 4, 6, 8 and 10 g), 5^{th} day