CHAPTER 2 THEORY AND LITERATURE REVIEW

This chapter consists of theory and literature review related to this research. The theory part describes the overview of the plastic mulch and its applications, urea and furfural characteristic, biodegradable polymer features, furfural-urea complex preparation and product characterization techniques including Nuclear Magnetic Resonance Spectroscopy (NMR), Fourier transform infra-red absorption spectroscopy (FT-IR), Attenuated total reflectance/fourier transform infrared (ATR), UV-visible spectrometer and Thermal gravimetric analysis and Differential scanning calorimeter (TGA/DSC). The literature review part focuses on the controlled release, the plastic mulch application and also the method to increase farming efficiency. Additionally, the condensation of the furfural with urea in aqueous and heterogeneous phase is mentioned together with the biodegradation of PBSA.

2.1 Theory

This section describes the overview of the agricultural plastic mulch, controlled release in agriculture and the nature of urea and furfural including the detail of biodegradable polymers, poly(butylene succinate-co-butylene adipate) or PBSA. The extrusion process that is used to extrude the biodegradable polymer mixed with the complex of furfural-urea is also presented together with the preparation of the furfural-urea complex. Moreover, the characterization techniques that are used to identify the product are also mentioned.

2.1.1 The overview of the agricultural plastic mulch

For many decades, mulching is a technique which has been used by farmers. Mulches can be classified into organic or inorganic. Organic mulches are derived from plant and animal materials. Those most frequently used include plant residues such as straw, hay, peanut hulls, leaf mold, and compost; wood products such as sawdust, wood chips, and shavings and animal manures. Organic mulch properly utilized can perform all the benefits of any mulch with the possible exception of early season soil warming. However, natural mulch materials are often not available in adequate quantities for commercial operations. Consequently, inorganic mulch is invented to facilitated farming industry. Inorganic mulch includes plastic mulch and accounts for the greatest volume of mulch used in commercial vegetable production.

The plastic mulch is introduced over many decades for greenhouse covering, fumigation and especially mulching as agricultural applications of polymers. Many polymers are utilized in different applications which include soil conditioning, seed coating, farm protection and also the controlled release of nutrients and nematocides. In addition, the interest of degradable plastics such as agricultural mulches is now a popular issue. Typically, mulches are used as weed prevention, soil temperatures increases and even

moisture conservative. If plastic mulches are left in the farm, this can cause problems during harvesting or cultivating operation in the next year. Removal and disposal are inconvenient and also costly. Therefore, the development of biodegradable or photodegradable with short service lifetimes is studied. Only a few of degradable polymers have been commercialized from the whole polymer types that could be designed for controlled degradation.

The plastics used for agricultural mulch are generally low density polyethylenes, polyvinyl chloride, polybutylene or copolymers of ethylene with vinyl acetate. A particularly interesting photodegradable system consists of a mixture of ferric and nickel dibutyldithiocarbamates, the ratio of which is adjusted to provide protection for specific growing periods. At the end of a growing season, the plastic will begin to photodegradė. Some additive systemsare proposed for this application including a combination of substituted benzophenones and titanium or zirconium chelates. The principal commercial degradable mulch is photodegradable poly(1-butene). Degradable mulches should break down into small pieces when passing through harvesting machinery without difficulty and do not interfere with subsequent planting. Effective fumigant mulches require reduced-porosity films which reduce the escape of volatile chemicals, i.e. nematocides, insecticides, herbicides, etc., and therefore allow lower application rates [5].

2.1.2 Controlled release of agricultural chemicals

Controlled release (CR) is a method that biologically active chemicals are made to serve a target species at a specified rate and for a predetermined time. The polymer is presented to control the rate of delivery, mobility, and period of effectiveness of the chemical component. Chemicals that are used in a small amount for a given time period is a principal advantage of CR formulations. Thus, lowering the impact on non-target species and limiting leaching, volatilization, and degradation are considered. The macromolecular nature of polymers is the key to limit chemical losses by these processes. There are two categories of CR polymeric systems. In the first category, the active agent is dissolved or encapsulated by the polymeric matrix or coating. Generally, release occurs by the biological or chemical breakdown of the matrix or diffusion processes. In the second category, the active agent in the polymer acts as part of the macromolecular backbone or pendent side chain. Release is resulted from biological or chemical cleavage of the bond between the bioactive agents and the polymer.

Physical systems that incorporate agricultural chemicals include microcapsules, physical blends, and dispersions in plastics. Kinetic models for release in different types of devices have been developed. Starch, cellulose, chitin, alginic acid, and lignin are among the natural polymers used in CR systems. The reason why these compounds are chosen is the advantages of being abundant, relatively inexpensive, and biodegradable. However, they have the one significant disadvantage of being insoluble in standard solvents suitable for encapsulation, dispersion, and formulation.

Fertilizer is one of the largest applications for CR technology in agriculture. Urea, a significant nitrogen source, easily reacts with formaldehyde to form a polymer. Subsequent hydrolysis of the polymer yields urea. Therefore, this is a simple and inexpensive system for CR [5].

2.1.3 Furfural

Furfural is a clear, colorless liquid with a boiling point of 162°C and a freezing point of 36.5°C,at 760 mm mercury. Furfural is miscible with most common organic solvents but is only sparingly soluble in water. Furfural is an aromatic aldehyde but the aromatic properties of the furan ring are different from those of the benzene ring. The furan ring has less aromatic character than the benzene ring because stabilization energy of furan is smaller than that of benzene. Hence, furan compounds in general would be more reactive in ring addition reactions than the corresponding benzene compounds.

Furfural is typically produced from renewable resources as agricultural waste such as corncobs, cotton seed hulls, rice hulls, or oat hulls, as well as from wood wastes. The raw materials are heated in a digester with a strong inorganic acid in order to hydrolyze the pentosansto pentoses. The pentoses undergo cyclodehydration to form furfural, which is recovered from the digester by steam distillation. Furfural is used for the production of furan, furfuryl alcohol, tetrahydrofuran, and their derivatives as a solvent for selectively separating saturated from unsaturated compounds in petroleum lubricating oil, gas oil, and diesel fuel. Moreover, it is used in the extractive distillation of butadiene and other C4 hydrocarbons. In the manufacture of synthetic rubber, it acts as a resin solvent and wetting agent in various other industrial processes [6].

Furfural can be produced from 2 different types of technologies including one-stage and two-stage technologies. In one-stage technology, depolymerization of pentosans in xylose and dehydration to furfural occur simultaneously. In two-stage technology, a dissolution and depolymerization of pentosans occur under mild conditions, followed by dehydration of xylose to furfurai. The advantage of two-stage technology is based on the fact that the residual lignocellulose is less degraded and can be used for conversion to other chemicals (glucose, ethanol, phenols, etc.) in a subsequent step. The industrial process usually employs the one-stage approach and the resulted residue is used for steam production [7].

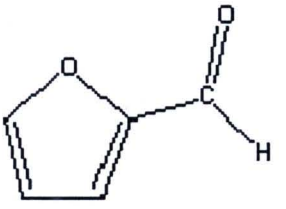


Figure 2.1 Molecular structure of furfural

2.1.4 Urea

Urea, the lowest known cost of nitrogen-contained materials, is the most widely used solid N fertilizer in the world. Its molecular structure is shown in Figure 2.2. The production of urea fertilizer involves controlled reaction of ammonia gas (NH_3) and carbon dioxide (CO_2) with elevated temperature and pressure. Urea is used in many different ways to provide N nutrition for plant growth. It is typically mixed with soil or applied to the soil surface. It sometimes may be dissolved in water and applied to soil as a fluid due to its high solubility. After urea contacts soil or plants, a naturally enzyme termed urease begins to convert the urea back to NH_3 rapidly in a process called hydrolysis. During this process, the N in urea is susceptible to undesirable gaseous losses as NH_3. Many useful techniques can be used to minimize the loss of this valuable nutrient.

The concentration of biuret (NH_2-CO-NH-CO-NH_2) in urea is a special concern because of its phytotoxicity. About two percentages of biuret can be tolerated in most fertilizer programs. Some crops including citrus and pineapple is sensitive to biuret. Urea applied as a foliar spray should contain biuret less than 0.25%. Solutions made from urea containing 1.5% biuret are acceptable for foliar application on corn and soybeans. High concentration of biuret in urea should not be placed near or in the seed row.

Urea is ultimately biodegradable as it is biodegraded on the average of 93-98% in 24-hour cycle. The main mode of degradation is enzymatic mineralization. In soil and water, urea is expected to biodegrade rapidly to ammonia and bicarbonate in a suitable temperature. Ammonia is a volatile gas in alkaline solutions. In natural waters, most ammonia appears in the form of ammonium, from which nitrogen is oxidized.

Additionally, urea is used in many industries for many functional uses such as adhesives, binders, sealants, resins, fillers, analytical reagents, catalysts, intermediates, solvent, etc. Furthermore, urea is also the key synthetic ingredient in the manufacture of some medicines [8].

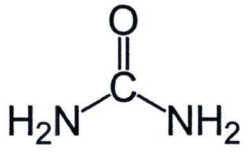


Figure 2.2 Molecular structure of urea

2.1.5 Biodegradable polymer

Biodegradable polymer is introduced to solve the environmental pollution problem as the disposal of conventional plastics are not incorporated into the carbon cycle and have decreased the landfill capacity because of their low degradability. A polymer having a lower melting point is generally more susceptible to biodegradation than the higher one.

Those with lower melting temperatures have more flexible chains which can fit into the active sites of the enzymes. Aliphatic polyesters are considered as the most promising materials used in biodegradable plastics. Poly(hydroxyalkanoate) (PHA), poly(lactic acid) (PLA), poly(-caprolactone) (PCL), and poly(butylene succinate-co-butylene adipate) (PBSA) are commercially produced as Biopol, LACEA, TONE, and Bionolle, respectively. Among these polymers, PBSA is considered as an alternative to conventional plastics because of its comparable mechanical properties and low production cost[9].PBSA can be processed in the field of textiles into melt blow, multifilament, monofilament, flat, and split yarn and also in the field of plastics into injection molded products [10].

Poly(butylene succinate) (PBS) and poly(butylenes succinate-co-butylene adipate) (PBSA) can be produced by diacids and diols with low production cost and mechanical properties similar to polyolefins. It can be molded into a variety of products using conventional equipment applicable to polyolefins. PBSA is more susceptible to biodegradation than PBS because of its lower crystallinity and more flexible polymer chains that can fit into the active sites of enzymes [11].

Figure 2.3 Molecular structure of poly(butylenes succinate-co-butylene adipate) (PBSA) [12]

2.1.6 Extrusion

Extrusion is used in all methods of polymer processing either forming or transporting and metering the molten plastic before it is formed. Extrusion is the process where a solid plastic or also called a resin, usually in the form of pellets, is continuously fed to a heated chamber and carried along by a feed screw within. The configuration of feed screw is critical to product quality. The polymer is conveyed, compressed, melted, and forced out of the chamber at a steady rate through a die. The melted polymer is then cooled immediately results in resolidification of that plastic into a different type of cross section depending on the die pattern.

The basic extruder is available in many different versions depending on the application and the materials being processed. First type of extruder is a single screw extruder which is generally used for simple extrusions using granules and pre-prepared compounds. The single screw extruder is one of the most basic forms of extruder that simply melts and forms the material. The other type of extruder is a twin-screw extruder. Twin-screw extruders are widely used for mixing, compounding, or reacting polymeric materials. The flexibility of twin screw extrusion equipment allows this operation to be designed in a wide variety of formats depending on the manufacturer, and all have been developed to meet specific market needs [13].

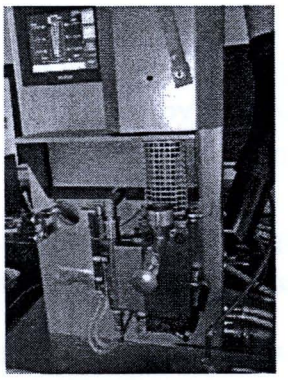


Figure 2.4 Twin screw extruder

2.1.7 Solvent casting

Solvent casting is a technique that polymer is dissolved in an organic solvent. When the solvent evaporates it creates a structure of composite material consisting of the particles together with the polymer. There are many advantages of this technology including uniform thickness distribution, maximum optical purity and extremely low haze. The films have excellent flatness and dimensional stability. The cast film can be processed in-line with an optical coating design. The tremendous growth of new liquid crystal display applications has incited the development of new materials and improved processes for solvent casting and coating techniques.

There are constraints on the types of polymer films for which solvent casting technology must or cannot be used. Relatively few materials can be processed into films by both methods – slot extrusion and solvent casting. In these cases, a cost-performance comparison decides. Extrusion cannot produce very thin films without stretching. On the other hand, very thick films are very costly to produce by solvent casting and lamination. In general, solvent-cast products are more expensive than extruded film to manufacture for several reasons:

-Slow production speed due to a slow solvent diffusion process

- Extra energy costs of solvent recovery

- Investments in facilities for handling solvents and dope solutions

On the other hand, the performance and, more specifically, the high quality of solvent cast films cannot be achieved using other processes.

2.1.8 Characterization techniques

1. Nuclear Magnetic Resonance Spectroscopy

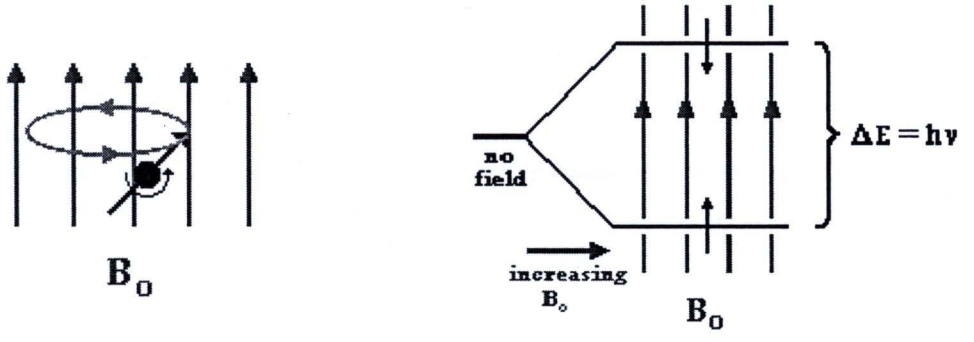
Nuclear Magnetic Resonance Spectroscopy known as NMR spectroscopy is used to determine the structures of molecules. Significant data can be obtained by measuring, analyzing, and interpreting the high-resolution NMR spectra recorded on the liquids of low viscosity. This technique relies on the magnetic properties of the atomic nucleus. There are 2 typically types of model. First model is the classical model. In classical model, many atoms spin on an axis as the positively charged nucleus. The spinning

charge creates a tiny magnetic field and it is forced by a strong external magnetic field to align itself with a compass needle in the earth's magnetic field. Because the nucleus has angular momentum, the torque exerted by the external field results in a circular motion called precession. The rate of this precession is proportional to the external magnetic field strength and to the strength of the nuclear magnet. This resonant frequency can be measured by applying a radio frequency signal to the sample and varying the frequency until absorbance of energy is detected.

For the quantum model, there are two quantum states which can be visualized as having the spin axis pointing "up" or "down". The energy of "up" state that aligns with the magnetic field is lower than of the "down" state which is opposed to the magnetic field. There is no possible state in between up and down state because of quantum phenomenon. The gap between the two quantum states is proportional to the strength of the external magnetic field. In the thermal equilibrium, a large population of nuclei slightly more than half will reside in a lower energy state, while slightly less than half will reside in the higher energy state. As in all forms of spectroscopy, it is possible for a nucleus in the lower energy state to absorb a photon of electromagnetic energy and be promoted to the higher energy state. The energy of the photon absorption is referred to the energy gab between two states (ΔE), and this energy corresponds to a specific frequency of electromagnetic radiation:

$$\Delta E = h\sqrt{} \qquad \text{eq. 2.2.1}$$

Where, h is Plancks constant
$\sqrt{}$ is the resonant frequency



Classic model Quantum model

Figure 2.5 The classical model and quantum model for NMR spectroscopy [14]

The resonant frequencies of some important nuclei are shown below for the magnetic field strength of a typical NMR spectrometer:

Table 2.1 The resonant frequency of a typical NMR spectrometer

Nucleus	Abundance	Sensitivity	Frequency
^{1}H	100%	1.0	200 MHz
^{13}C	1.1%	0.016	50 MHz
^{15}N	0.37%	0.001	20 MHz
^{19}F	100%	0.83	188 MHz
^{31}P	100%	0.066	81 MHz
^{57}Fe	2.2%	3.4×10^{-5}	6.5 MHz

The resonant frequency is proportional to the external magnetic field strength. The relative sensitivity is a direct result of the strength of the nuclear magnetic, and the effective sensitivity is further reduced for those nuclei which occur at low natural abundance [14].

Three types of spectral parameters are obtainable from NMR spectra including chemical shifts, indirect spin-spin couplings, and intensities. The chemical shift is caused by the magnetic shielding of the nuclei by their surrounding electrons. The resonant frequencies depend on the magnetic flux density, and this is the reason why line positions are never specified. A dimensionless quantity, the δ value, obtains the signal position relative to the reference compound and also relates to the measurement frequencies. Therefore, the δ value is independent of the spectrometer. This means that it can be directly used in comparison. The typically reference compound used in ^{1}H and ^{13}C NMR spectroscopy is tetramethylsilane (TMS). Since equivalent nuclei have the same resonant frequency, the effect of simplifying the spectrum in molecular symmetry is occurred.

For spin-spin couplings, the interaction between neighboring nuclear dipoles leads to a fine structure which the strength of this interaction is given by spin-spin coupling constant (J). The indirect spin-spin coupling is obtained when the coupling occurs through chemical bonds. The indirect spin-spin coupling is independent of the external field, and the coupling constants J are given in Hz. Moreover, couplings can be observed not only between the same species nuclei but also between different nuclei as a heteronuclear coupling. The most significant coupling is H,H coupling and C,H coupling. Only ^{1}H NMR spectroscopy can determine the signal intensities for each spectrum, but ^{13}C NMR spectra cannot be measured [15].

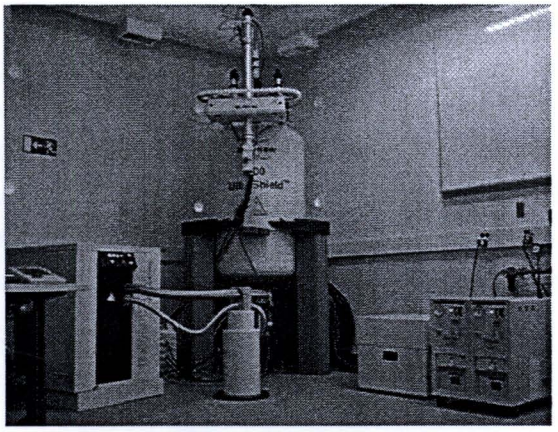


Figure 2.6 NMR spectroscopy equipment

2. Thermalgravimetric analysis(TGA) and Differential scanning calorimetry(DSC)

There are two common techniques in the thermal analysis categories which are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).These two methods are typically used to measure the material properties of organic polymers as a function of temperature or time in case that sample is subjected to the isothermal condition.

Differential scanning calorimetry (DSC) measures heat generated or consumed in a sample as a function of temperature or time. A small amount of a sample is placed on an aluminum pan and then heated or cooled in a controlled manner. A reference material, which is usually an empty aluminum pan, simultaneously undergoes the same program. There are two methods that can be used for the calorimetric measurements. In the first method, the difference in temperature between the reference material and sample can be measured when the same amount of heat is added to both. For the second method, the difference in the amount of heat added to both is measured when the temperatures for both the sample and reference are the same. The heat flow and temperature of the sample in two cases are monitored and compared with the reference material. The analysis is usually performed in an inert gas atmosphere such as nitrogen. The amount of energy absorbed (endotherm) or evolved (exotherm) as the sample undergoes physical or chemical changes is measured in calories as a function of temperature. Any material reactions involving changes in heat capacity are also detected.

Thermogravimetric analysis (TGA) measures the weight of a sample as a function of temperature and time. The sample is placed on a small pan as same as in DSC method with a microbalance connection. The sample is then heated in a controlled manner and/or held isothermally for a specified time. There is a reactive or inert gas around the sample such as nitrogen, air and oxygen. The heating program starts in an inert atmosphere and then switches to air at a certain point to complete the analysis. Weight changes observed at specific temperatures correlate to volatilization of sample components, decomposition, oxidation/reduction reactions, or other reactions or changes. As the TGA instrument measures the temperature and weight of the sample,

thermally activated events are recorded. These events are expressed as weight loss or weight change for a given time or temperature together with a rate of weight loss. The onset temperature for the weight loss is also recorded. These data correlate to information about such properties as: thermal stability, moisture or solvent content, additive or filler content, oxidation or decomposition temperatures and rate. Thermal events such as melting, glass transition, and other changes are not detected because there is no change in sample mass associated with these events [16].

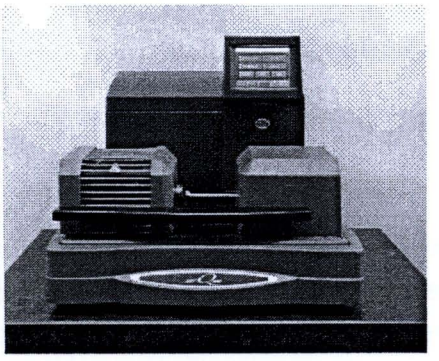


Figure 2.7 DSC/TGA equipment

3. Fourier transforms infra-red absorption spectroscopy (FT-IR)

FTIR is the most useful method for identifying chemicals that are either organic or inorganic from spills, paints, polymers, coatings, drugs, and contaminants. It can be applied to the analysis of solids, liquids, and gasses. It can identify unknown materials and determine the amount of components in a mixture. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. An infrared spectrum represents a fingerprint of a sample with absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms of the material. Each different material consists of a unique combination of atoms, this means that no 2 compounds can produce the exact same infrared spectrum. Furthermore, the size of the peaks represented in the spectrum is a direct indication of the amount of material present.

A background spectrum needs to be measured because it needs to be a relative scale for the absorption intensity. This is normally a measurement without any sample in the beam which will be compared to the measurement with the sample in the beam to determine the "percent transmittance". The results obtained from this technique express the spectrum which has all of the instrumental characteristics removed. This means that all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is the characteristic of the instrument itself [17].

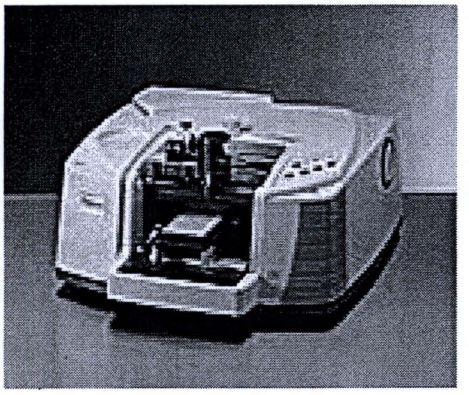


Figure 2.8 FT-IR equipment

4. Attenuated Total Reflectance/Fourier Transform Infrared

Attenuated total reflection using infrared Fourier transform (ATR) spectroscopy is considered as one of simple, direct, flexible and sensitive infrared technique. This method is introduced to solve the transmission infrared problem includes path length and concentration since all of the radiation is reflected. Recently, horizontal ATR is used instead of the traditional one in which a thin sample is clamped against the vertical face of the crystal. ATR technique involves the collection of radiation reflected from the interface between aqueous solution and a prism, in which the evanescent wave penetrated from the prism into the aqueous solution, is absorbed by substances in the aqueous solution. In addition, ATR also provides excellent quality data in conjunction with the best possible reproducibility of any IR sampling technique.

A good optical contact between the sample and the crystal is necessary while measuring the ATR. The accessories have devices that clamp the sample to the crystal surface and apply pressure. This technique works well with elastomers and other deformable materials, and also with fine powders. On the other hand, many solids give very weak spectra because the contact is confined to small areas. The effects of poor contact are greatest at shorter wavelengths where the depth of penetration is lowest. The issue of solid sample/crystal contact has been overcome to a great extent by the introduction of ATR accessories with very small crystals, typically about 2 mm across. The most frequently used small crystal ATR material is diamond because it has the best durability and chemical inertness. These small area ATR crystal top-plates generally provide only a single reflection but this is sufficient, given the very low noise levels of PerkinElmer's modern FT-IR spectrometers. Much higher pressure with limited force can now be generated onto these small areas. A much smaller area of contact is now required in comparison to the Horizontal attenuated total reflection or HATR units. As a result, spectra can be obtained from a wide variety of solid materials including minerals [18].

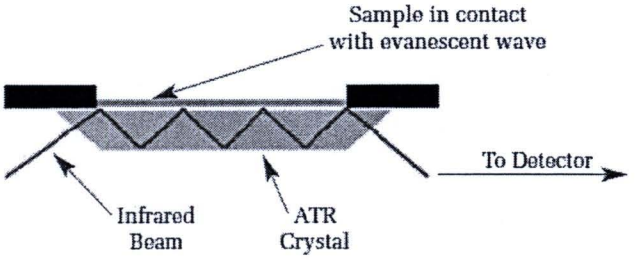


Figure 2.9 A multiple reflection of ATR system

5. Ultraviolet and visible absorption spectroscopy (UV-Vis)

Ultraviolet and visible (UV-Vis) absorption spectroscopy is a technique that measures the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. There are many advantages in UV-Vis spectroscopy including detection of eluting components in high performance liquid chromatography (HPLC), determination of the oxidation state of a metal center of a cofactor, or determination of the maximum absorbance of a compound prior to a photochemical reaction[19].Most organic compounds that absorb UV-VIS radiation contain conjugated pi-bonds. UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra are very useful for quantitative measurements but are limited for sample identification. The concentration of an analyzed solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

$$A = ebc$$

Where, **e** is a constant of proportionality, called the *absorbtivity*.

The components of UV-Vis consist of sources, wavelength selector, sample containers, detector and signal processor. Generally, the source must be more intense than that is required for UV-Vis. The magnitude of the emitted radiation is directly proportional to the power of the source. Filter fluorometers often employ a low-pressure mercury vapor lamp. This source produces intense lines at certain wavelengths. One of these lines will usually be suitable for excitation of a fluorescent sample [20].

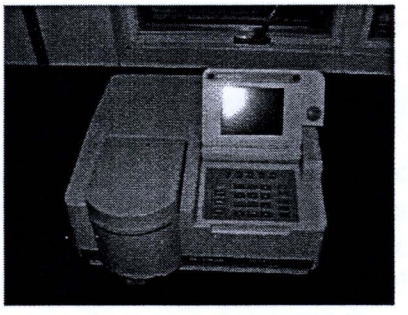


Figure 2.10 UV-vis spectroscopy

2.2 Literatures review

Martınez-Garcıa et al. [4] studied the condensation of furfural with urea in aqueous and heterogeneous phases. The experiments used different furfural-urea molar ratios. The products were characterized through ^{1}H ^{13}C and ^{15}N NMR, X-ray diffraction, FTIR, DTA, TG, and DSC. The results revealed that the reaction in the homogenuous phase was faster than the reaction in the heterogeneous phase. Moreover, The NMR spectra indicated that product always was difurfurilidentriurea in whatever molar ratio of furfural-urea used in syntheses. In the X-ray diffraction, the synthesized products obtained from the heterogeneous phase were more crystalline than the products obtained from the aqueous phase. Also, the crystallinity increased proportionally to the molar ratio of urea/furfural. The thermal analysis indicated that the product was stable in the temperature lower than 160°C and the decomposition was achieved under endothermic reaction.

Schneider et al. [21] studied the methods of furfural-urea modification of woods and also particularly the invention related to polymerization and impregnation of furfural-urea under high weight percent gain into wood conditions. The condensation was carried out by two different methods: (1) in the presence of water, catalyzed by HCl, and (2) without a solvent. The results revealed yield from the reaction changed with time for the syntheses conducted in aqueous and heterogeneous phases.

Amarasekara et al. [22] studied the condensation of renewable resources based monomer 2,5-diformylfuran (DFF) and urea at110°C by melting a solid mixture. The resin from the condensation process was characterized by elemental analysis, ^{1}H, ^{13}C and ^{1}H–^{1}H COSY NMR, IR, UV, TGA, and DTA. The result revealed that the condensation part produced an insoluble and crystalline polymer resin with 90% yield. The structure of the polymer is shown to have the structural unit 3 with a cross-linked structure by a combination of spectroscopic methods and elemental analysis.

Anikwe et al. [23] studied the effect of two tillage systems and plastic film mulch on soil properties and cocoyam growth and yield on a Typicpaleudult in southeastern Nigeria. The results indicated that plastic mulches and tillage techniques significantly affected the growth characteristics and yield of cocoyam. Moreover, the different color of plastic mulch also affected corn emergence, height of plant, soil temperature, leaf area index (LAI) and yield. The tilled black plastic-film mulched treatment also had the highest corm yield. Furthermore, plastic-film mulch and tillage techniques could be used to manipulate the soil environment of cocoyam for profitable production.

Mogel et al. [24] studied the reduction of pesticides, herbicides, and other biologically active agents used in modern agricultural crop management. One method for reducing the amount of those agents is to encapsulate or incorporate the active agent into some form of plastic. By incorporating the active agent into the plastic, the active agent diffuses slowly, but continuously. This also decreases the amount of active agent used. In addition, the incorporation of the biological agent into plastic serves the role of the

biological protection as well as providing slow release. The rate of release of the substance is determined by the properties of the polymer itself.

Chen et al. [25] studied the new type of slow release membrane-encapsulated urea fertilizer with starch-g-PLLA as biodegradable materials. Urea was individually encapsulated within the starch matrix. The results revealed that the invention of hydrophobic PLLA reduced the release rate of urea. In addition, the release rate of urea could be controlled by graft efficiency. From the scanning electron microscope, the modified starch products for controlled release were suggested for widely potential application in agricultural industry as fertilizer carrier.

Ni et al. [26] studied the preparation of double-coated, slow release, and water-retention urea fertilizer in order to reduce environmental pollution derived from excessive nitrogen used as fertilizer. The coating material consisted of ethylcellulose and crosslinked poly(acrylic acid-co-acrylamide) as an inner and outer coat, respectively. The biodegradation of EC coating in soil was assessed by differential scanning calorimeter (DSC) measurements. The results revealed that the product contained 21.1% of nitrogen and its water absorbency was 70 times its own weight in tap water. Moreover, the glass transition temperature (Tg) of EC coating decreased with the time prolonged, which indicated the biodegradability of EC coating in soil. These studies showed that the product with good slow-release and water-retention properties, being environmentally friendly, would find good application in agriculture and horticulture.

Thomus et al. [27] studied the alternative system that used various colored plastic mulches with Telone C35 (63.4% 1,3-dichlropropene, 34.7% chloropicrin, 1.9% inert ingredients) to control weeds through wavelength selective plastic mulches. Furthermore, fungi weeds, and nematodes are also controlled by chloropicrinand 1,3-dichloropropene. The mulches tested were blue virtually impermeable film (VIF), black VIF, black polyethylenefilm (PE), as well as blue, green, olive, brown, and metalized PE. The results indicated that there was no direct correlation between the amounts of light transmitted through colored mulch with tomato yield per plant. Moreover, the use of fumigation with plastic mulches led to an average increase of 40% in crop yield compared to non-fumigated beds. It could be concluded that metalized PE mulch would maximize weed control and crop yield without any use of pesticide, fungicide, or herbicide.

Sato et al. [28] studied the changed behavior in the chemical structures of a biodegradable aliphatic copolyester, poly(butylene succinate-co-butylene adipate) (PBSA). The sample was investigated by Py-GC during the soil burial degradation. The evaluation of the degree of PBSA biodegradation can be measured by the variation of the relative yields of the fatty-acid esters. Furthermore, the evaluation of the local structural changes for the biodegraded PBSA film samples was collected from the relative yields of these specific esters observed on the programs.

Zhao et al. [11] studied the behavior and biodegradation mechanism of poly(butylene succinate-co-butylene adipate) (PBSA) by Aspergillusversicolor isolated from compost.

The results revealed that more than 90% of PBSA film was absorbed within 25 days. The molecular weight characterized by gel permeation chromatography (GPC)rapidly decreased. Scanning electron microscopy (SEM) expressed the holes and many of cracks scattering on the film surface. The analyses of proton NMR and differential scanning calorimeter (DSC) indicated that the adipate part preferred degradation while the succinate units are relatively recalcitrant to A. versicolor.