CHAPTER II
## THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Smart Card

Smart card is a type of chip card that a plastic card was embedded with a computer chip that stores and transacts data between users . The data is associated with either value or information or both and is stored and processed within the card's chip, either a memory or microprocessor. The card data is transacted via a reader that is one part of a computing system.

The size of the card is determined by an international standard (ISO 7816) which widely use for credit card. The card have dimensions of 85.60 × 53.98 mm and thickness 0.76 mm. Smart Card contains a security system with tamper-resistant properties, secure cryptoprocessor, secure file system, human-readable features. Card data is transferred to the central administration system through card reading devices, such as ticket readers, ATMs etc.

There are two types of smart card. First, Contact smart cards have a contact area, comprising several gold-plated contact pads, that is about 1 cm square. When inserted into a reader, the chip makes contact with electrical connectors that can read information from the chip and write information back. Second type is the contactless smart card, in which the chip communicates with the card reader through RFID induction technology. These cards require only close proximity to an antenna to complete transaction. They are often used when transactions must be processed quickly or hands-free, such as on mass transit systems, where smart cards can be used without even removing them from a wallet. There are many commercial materials which are widely used for smart card body; i.e., PVC (polyvinyl chloride), ABS (Acrylonitrile Butadiene Styrene), PC (polycarbonate) and PET (polyethylene terephtarate) (J. Markarian 2004).

2.2 Type of Smart Card Body

2.2.1 Polyvinyl Chloride (PVC)
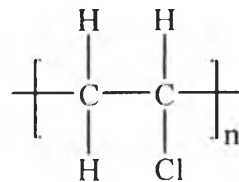
Figure 2.1 PVC structure.

PVC is the least expensive of the main card body materials. It is used for both contact and contactless cards, but generally has a shorter life expectancy than other card body materials, due to a lower resistance to heat, UV and bending stress, which can cause premature delamination and module separation. PVC is generally used for financial cards with a life expectancy of 3-5 years. The main durability issues of PVC include: surface wear (scratching and print erosion), de-lamination where finishing layers begin to separate, effects of physical stress (flexing and twisting) on the card body, chemical damage (from petrol, nail varnish, cooking oil, etc.), UV light causing print finish deterioration, and weaknesses caused by certain personalization features (embossing, laser engraving).
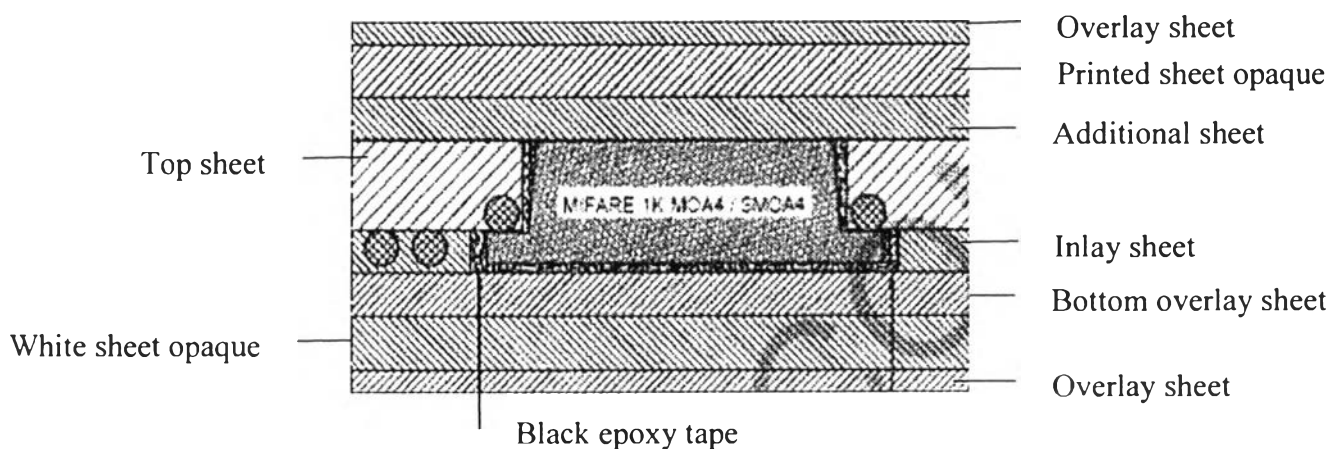
**Figure 2.2** PVC card's composition. (data from Smartrac Technology LTD)

2.2.2 Acrylonitrile Butadiene Styrene (ABS)
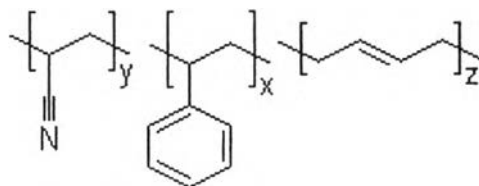
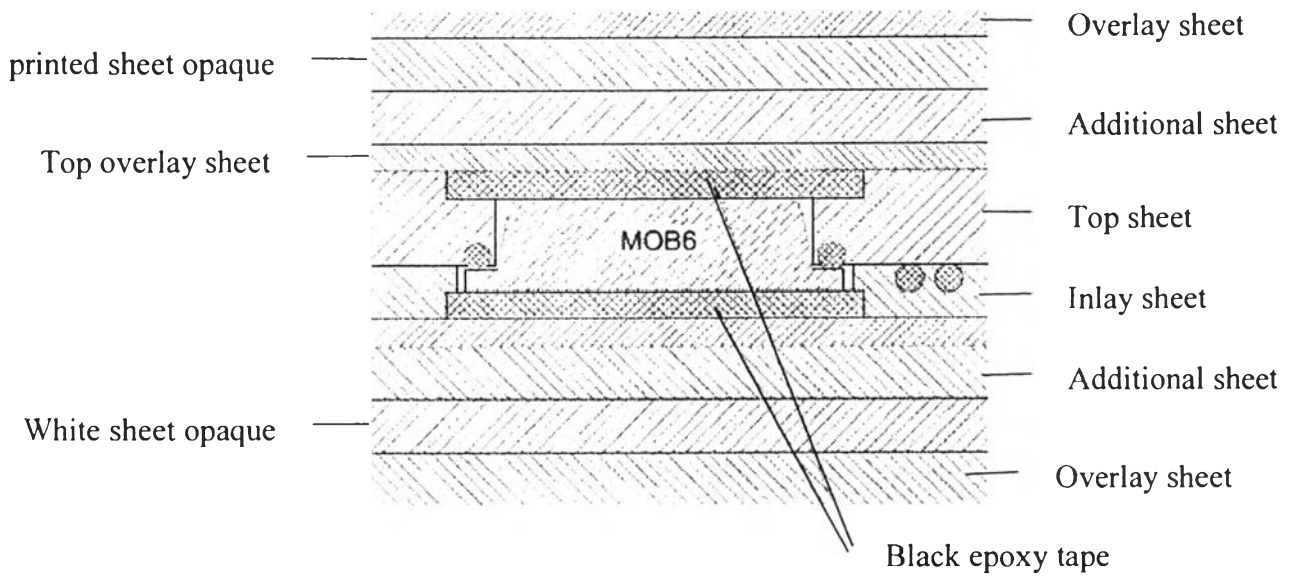**Figure 2.3** ABS structure.

ABS is an amorphous thermoplastic that is distinguished by its stability and resistance to temperature. ABS is often used for card for mobile telephone. It can be processed both in sheet form and injection molding.

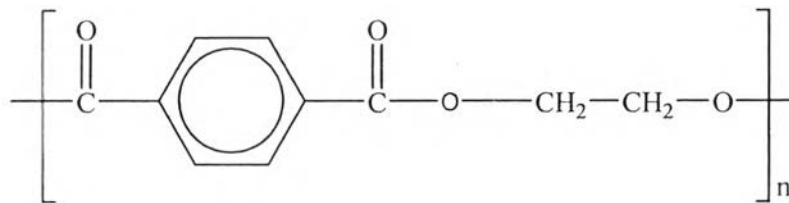## 2.2.3 Polycarbonate (PC)
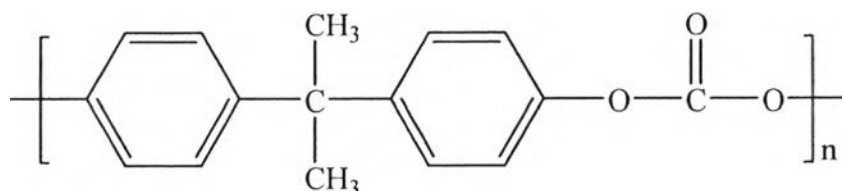
Figure 2.4 PC structure.

PC is a more rigid card body material which has a much higher resistance to damage from heat, flexing and UV. However, PC can have a tendency of brittleness which can be adversely affected by frequent automated handling, causing shatter cracks and is less resistant to caustic solutions and certain solvents.

printed sheet opaque

Top overlay sheet

White sheet opaque

Overlay sheet

Additional sheet

Top sheet

Inlay sheet

Additional sheet

Overlay sheet

Black epoxy tape

Figure 2.5 PC card's composition. (data from Smartrac Technology LTD)

2.2.4 Polyethylene Terephtarate (PET)

Figure 2.6 PETG structure.

PET, PETF (polyester film) and PETG are special materials that have been developed to enhance specific strengths or reduce certain weaknesses. These derivative materials are often combined with specialty card body substrates to significantly enhance the physical durability of cards for specific applications. In particular to reduce the incidence of antenna connection breaks and contact plate separation caused by flexing and bending of the card body. For example, PETF is a PET derivative that has very high thermal stability, mechanical strength and chemical inertness. In fact, PETF has one-third the tensile strength of steel and can withstand temperatures of up to 200° C and has high resistance to solvent.

White sheet opaque

White sheet opaque

Overlay sheet

Pre-lamina

Overlay sheet
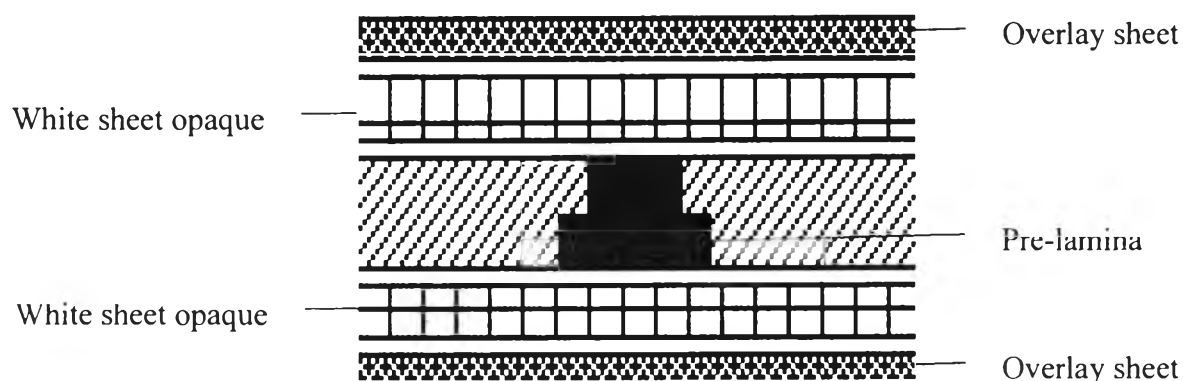
Figure 2.7 PETG card's composition. (data from Smartrac Technology LTD)

2.3 Polymers Degradation and Stability

Polymers are susceptible to attack by a wide variety of naturally occurring and man-made agents. Some of them are environmental agents and examples of polymers that is particularly susceptible to their action. In most cases, such environmental action is deleterious. For example, UV radiation and ozone can seriously degrade the unsaturated elastomers used in rubber tires. This degradation will limit the lifetime of the tire and could cause catastrophic failure. In practice, UV and ozone resistance is provided by adding various filler and stabilizers to tire formulation (D. G. Legrand, 2000), (J. R. Fried, 2003).

Polymers can degrade by exposure to high temperature (thermal degradation), shear action (mechanodegradation), oxygen and ozone, electromagnetic (γ, UV) and ultrasonic radiation, moisture (hydrolysis), and chemical agents. Often, multiple exposures, such as a combination of moisture and heat or oxygen and light (photooxidation), can result in accelerates deterioration. Deterioration of plastics to normal environmental conditions is called weathering. Factors contribute to weathering include radiation (UV, visible, and near-infrared), moisture, temperature cycling, and wind. Factors regulating on the degradation of plastics are the effects of temperature, oxygen, moisture, radiation, and chemical agents (J. R. Fried, 2003).

2.3.1 Thermal Degradation

In general, vinyl polymers are particularly susceptible to thermal degradation, which can occur either by chain scission involving the breakage of the backbone bonds to yield free radical segments or by non-chain scission, involving the elimination of a small molecule from a substituent group and subsequent double-bond formation.

2.3.1.1 Chain Scission

Chain scission can occur by one of three mechanisms. These include random degradation, where the chain is broken at random sites; depolymerization, where monomer units are released at an active chain end; and weak-link degradation, where the chain breaks at the lowest-energy bonds. In addition to thermal energy, degradation may be initiated by photochemical action, irradiation, or mechanical action.

2.3.1.2 Non-chain Scission Reactions

One example of a common non-chain scission reaction is dehydrohalogenation which results from the breakage of a carbon-halogen bond and the subsequent of hydrogen halide. The most important example of a polymer that degrades by dehydrohalogenation is poly(vinyl chloride) (PVC). PVC undergoes dehydrochlorination at temperatures near and above its T_g (87°C) to yield hydrogen chloride and ultimately a polyene (i.e., conjugated double-bond) structure, which is accompanied by intense color formation. The presence of hydrogen chloride will accelerate the dehydrochlorination process, resulting in further property deterioration. PVC can be stabilized by adding compounds that interfere with the degradation process, neutralize hydrochloric acid as it is formed, trap free radicals, or react with double bonds to prevent subsequent chain scission. Commercial PVC resins usually contain organo-tin or similar thermal stabilizers. Another example of a commercial polymer that undergoes a non-chain scission reaction at high temperatures is poly(vinyl alcohol) (PVA). Thermal degradation liberates acetic acid and results in polyene formation as in the case of PVC (C. E. Wilkes *et al.,* 2005), (J. R. Fried, 2003).

2.3.1.3 Strategies for Thermally Stable Polymers

Many flame-retardant additives as well as co-monomers designed to improve the fire resistance of certain polymers are thermally labile and, therefore, the thermal stability of the polymer can be reduced. For use at high temperatures for extended periods of time, the most successful polymers are those with highly aromatic structures, especially those with heterocyclic rings. Resonance stabilization results in high main-chain bond strength and consequently high thermal stability.

Polymers having high-temperature stability as well as other high-performance properties are examples of specialty polymers designed for limited use in aerospace, electronics, and other applications. Unfortunately, the same factors that contribute to high-temperature stability of these polymers also translate to high T_g, high melt-viscosity, and insolubility in common organic solvents, which make these polymers difficult or impossible to process by usual methods, such as extrusion and injection molding. Successful commercialization, therefore, always requires some compromise between thermal properties and processability.

2.3.2 Oxidative and UV stability

With the exception of fluoropolymers, most polymers are susceptible to oxidation, particularly at elevated temperature or during exposure to ultraviolet light. Oxidation usually leads to increasing brittleness and deterioration in strength. Generally, the mechanism of oxidative degradation is free radical and is initiated by the thermal or photolytic cleavage of bonds. The free radicals then react with oxygen to yield peroxides and hydroperoxides.

Oxidative degradation of saturated polymers can also occur through a complex series of reactions that involve the intermediate formation of peroxy radicals. Polystyrene is especially susceptible to photooxidative degradation. In this case, UV radiation is absorbed by the phenyl group, which can transfer the energy to nearby units along the polymer chain. Cleavage of the main chain can then occur with carbonyl-group formation. The result is yellowing and embrittlement of the plastic.

Commercial antioxidants include organic compounds like hindered phenols and aromatic amines, which act as free-radical scavengers, as well as agents

that serve to suppress hemolytic breakdown, such as organic phosphites. Effects of UV radiation may be reduced by incorporating additives, such as carbon black widely used in tire manufacture, that screen wavelengths in the UV range from 300 to 400 nm. Transparent thermoplastics like polycarbonate can be protected against yellowing and embrittlement from UV light by incorporating compounds, such as benzophenone derivatives, that have a high extinction coefficient in the UV range and are able to convert absorbed radiation into heat without chemical change.

2.3.3 Chemical and Hydrolytic Srability

2.3.3.1 Solvent Crazing and Cracking

Virtually all thermoplastics in contact with organic liquids and vapors will fail at lower levels of stress or strain even if the interacting chemical is not ordinarily considered to be a solvent for the polymer. The effect of these chemicals is believed to be due to localized plasticization that allows the development of crazes or cracks at reduced stress.

2.3.3.2 Hydrolysis

Many polymers are susceptible to degradation due to the effect of water, particularly under acidic conditions. These include some naturally occurring polymers, such as polysaccharides and proteins, as well as some synthetic polymers, principally condensation polymers such as polyesters and polyamides. In general, vinyl polymers are not susceptible to hydrolysis. Factors that influence the susceptibility of a given polymer to hydrolysis include water permeability and solubility that are determined by the chemical structure of the polymer and its physical state (e.g., crystallinity, glass-transition temperature, etc.). Autocatalysis of hydrolysis is possible if acidic or basic group are produced by the polymer breakdown as in the case in the case of polymers.

2.3.4 Effects of Radiation

Many polymers are susceptible to degradation and cross linking upon exposure to high-energy ionizing radiation (radiolysis) such as γ-radiation, electron beams, and X-rays. Sometimes, these effects can be used to an advantage. For example, integrated circuits can be prepared by microetching a polymeric coating of a silicon chip by electron-beam irradiation. The exposed silicon can then be doped. Radiation, particularly γ- and electron-beam radiation, can also be used to

prepare graft copolymers. Radiation can also be used to polymerize a monomer in the solid state and to modify surfaces for adhesive bonding. In other cases, such as the use of plastics in space vehicles, nuclear power plants, and γ-sterilized medical disposables, polymers and composites selected for these applications must have good resistance to radiation. For example, it has been estimated that the total dosage of radiation for an object spending 30 years in space orbit is on the order of 10 mrad. Sterilization of medical disposables such as syringes, surgical gowns, and labware by γ-irradiation has become increasingly important due to the limitations of other methods, such as the inefficiency of steam sterilization and the suspected carcinogenesis of ethylene oxide used in "cold" sterilization.

Some polymers such as polystyrene and polysulfone are very radiation resistant, but others such as polypropylene will readily degrade upon irradiation. In general, polymers with aromatic rings such as polystyrene, aromatic polyamides, and polysulfones are extremely radiation resistant, as are thermosets such as epoxies, phenolics, and urethanes. Fibers that have good radiation resistance include poly(ethylene terephthalate) and aromatic polyamides. Among elastomers. Polyurethanes have particularly good radiation resistance (J. R. Fried, 2003).

2.3.5 Mechanodegradation

Polymer degradation can also from the application of stress such as high sheer deformation of polymer solutions and melts. In the case of solids, stress-induced degradation may result from comminition, machining, stretching, fatigue, tearing, abrasion or wear. Mechanodegradation is particularly severe for high-molecular weight polymers that exist in a highly entangled state. The result of stress-induced degradation is the generation of macroradicals originating from random chain rupture.

2.4 Effect of Exposure

All of the polymer products are attacked by ultra-violet radiation and products made using these materials may crack or disintegrate. The ultra-violet degradation or photodegradation is a common problem in polymer products exposed to sunlight.

Testing of polymer stability examines either process stability or heat and light stability of the end-use product. Process stability is typically measured in a static oven test or a process-simulation. These tests gauge color development and physical properties over time as a measure of how well the additive package protects the polymer from degradation. Weathering or light stability is tested either in a laboratory weathering chamber that provides accelerated, simulated exposure or in actual outdoor exposure. In simulated weathering, polymer test pieces are placed in a laboratory weathering chamber and exposed to light from xenon arc or fluorescent UV lamps. Moisture can be added through humidity control or water spray. Experts from Atlas Material Testing Technology say that xenon arc tests have better correlation with outdoor weathering tests (J. Markarian, 2004).

The most appropriate test and light source depends on the material and its failure mode (Gadomski, international marketing manager at Q-Panel). For vinyl siding, fluorescent UV systems provide a more realistic simulation because moisture can be added through condensation on the polymer part. Required test protocols, including light source, are varied by country and by application. For example, weathering test guidelines for PVC window profiles typically ask for extended testing period equivalent to five years, with specific conditions such as moderate or extreme climate, notes Atlas. Five years outdoor weathering is equivalent to 4000 to 6000 hours on a xenon instrument. While weatherometer testing is useful for comparing relative performance of various additive packages and may be sufficient for approval in some applications, other applications require outdoor weathering testing for approval. New chemistries are typically tested in two or more different environments. Hot, humid Florida and the Arizona desert are considered primary benchmarks. During a weathering experiment, polymer color and physical property retention, impact strength and tensile properties are monitored. Whitening of the surface can be observed in outdoor weathering tests. Whitening may occur in humid environments, and is particularly obvious on darker-colored parts (J. Markarian, 2004), (W.R. Schaeffer *et al.,* 2004).

The North American Vinyl Siding Institute (VSI) standards currently call for two years of outdoor weathering in subtropical, desert, and northern industrial climates. VSI is considering an accelerated, simulated ageing program that would

grant temporary certification while outdoor testing results were pending. (J. Markarian, 2004), (W.R. Schaeffer *et al.,* 2004).

Materials exposed outdoors receive sunlight at varying temperatures, so an irradiance-weighted effective temperature may a good way to relate exposure conditions to each other. The effective temperature defined in this way depends on the temperature sensitivity of the material, which is the activation energy. However, E. Picket *et al.* (2009) have found that the results are relatively insensitive, which should encompass the range of many materials. They find the annual effective ambient air temperature and effective of temperature in black panel in many areas in United states.

Effective temperatures during outdoor exposures are lower than the temperature samples usually encounter during xenon arc weathering, making Arrhenius rate correction an essential part of lifetime prediction. Typical xenon arc exposures are carried out at temperatures more representative of the maximum outdoor sample temperatures that occur for only very brief periods during the year. While materials have to survive the conditions and should be tested to ensure, the effective temperature is appropriate for calculating the service lifetime. (E. Picket *et al.*, 2009)

Various PVC textile coatings have been comparatively tested in QUV and Weather-O-Meter (WOM) accelerated weathering chambers and in Florida tropical climate. The degradation has been measured by the variation of the IR optical density at 1780 cm. For all samples the WOM weathering is representative of the different forms of outdoor weathering degradation with an acceleration factor of some units. The QUV weathering is often representative of outdoor weathering with a greater than ten acceleration factor but for a sample which is rapidly outdoor degraded, the QUV chamber results showed that the sample is highly resistant to degradation. This contradiction can be explained by the absorption frequency of the single UV stabilizer corresponding to the emission frequency of the QUV lamps. A similar comparative aging study of differently stabilized and plasticized PVC laboratory films displays another case of non representativeness of the QUV weathering chamber. (E. Mathieu *et al.*, 1996)

E. Mathieu *et al.* (1996) studied in many plasticized PVC samples, the WOM weathering is representative of the different forms of outdoor weathering degradation with an acceleration factor of some units however the degradation acceleration is not as large as that obtained with the QUV for samples for which the latter causes an aging which is representative of reality. The study of laboratory plasticized PVC films has again shown that the QUV chamber is not representative. The results suggest that the presence of thermal stabilizers can affect photostability.

Furthermore J. Maatta *et al.* (2007) studied in Effect of plasticizer and surface topography on the cleanability of plasticized PVC materials, PVC plasticizers influence the properties of plasticized PVC products. In this study the effect of plasticizer and its amount on the water contact angles, recurrence accuracy of microstructures and cleanability of plasticized PVC were examined. The amount of plasticizer did not influence the water contact angles but the cleanability was enhanced when less plasticizer was added. The recurrence accuracy of the microstructure was reduced with more plasticized surfaces, in other words if the amount of plasticizer was increased.

2.5 MATLAB Application and Equation

MATLAB or matrix laboratory is a high-level language and interactive numerical computing software package for scientific, engineering and economic computation. MATLAB was developed by MathWorks, MATLAB enables to perform computationally intensive tasks faster than with traditional programming languages such as C, C++, and Fortran. MATLAB integrates numerical analysis, matrix computation, signal processing and graphics in an easy-to-use environment where problems and solutions are expressed just as they are written mathematically (Gilat, A., 2005).

Parametric fitting involves finding coefficients (parameters) for one or more models that you fit to data. The data is assumed to be statistical in nature and is divided into two components: a deterministic component and a random component.

$$data = deterministic\ component + random\ component \qquad (2.1)$$

The deterministic component is given by a parametric model and the random component is often described as error associated with the data.

$$data = model + error \tag{2.2}$$

The model is a function of the independent (predictor) variable and one or more coefficients. The error represents random variations in the data that follow a specific probability distribution (usually Gaussian). The variations can come from many different sources, but are always present at some level when dealing with measured data. Systematic variations can also exist, but they can lead to a fitted model that does not represent the data well.

The model coefficients often have physical significance. For example, collected data that corresponds to a single decay mode of a radioactive nuclide degradation property, and estimate the half-life ($T_{1/2}$) of the decay. The law of radioactive decay states that the activity of a radioactive substance decays exponentially in time. Therefore, the model to use in the fit is given by

$$y = y_0 e^{-\lambda t} \tag{2.3}$$

Where y_0 is the number of nuclei at time $t = 0$ or initial state.

λ is the decay constant.

The data can be described by

$$data = y_0 e^{-\lambda t} + error \text{ or } y = y_0 e^{-\lambda t} + error \tag{2.4}$$

Both y_0 and λ are coefficients that are estimated by the fit. Because $T_{1/2} = \ln(2)/\lambda$, the fitted value of the decay constant yields the fitted half-life. However, because the data contains some error, the deterministic component of the equation cannot be determined exactly from the data. Therefore, the coefficients and half-life calculation will have some uncertainty associated with them. If the uncertainty is acceptable, the data was fit. If the uncertainty is not acceptable, then take steps to reduce it either by collecting more data or by reducing measurement error and collecting new data and repeating the model fit.

In other situations where there is no theory to dictate a model, also modify the model by adding or removing terms, or substitute an entirely different model.

Exponential equations are often used when the rate of change of a quantity which is proportional to the initial amount of the quantity. If the coefficient

associated with e is negative, y represents exponential decay. If the coefficient is positive, y represents exponential growth.

$$y = ae^{bx} \tag{2.5}$$

$$y = ae^{bx} + ce^{dx} \tag{2.6}$$

For example, a single radioactive decay mode of a nuclide is described by a one-term exponential as seen in eq. (2.5). a is interpreted as the initial number of nuclei, b is the decay constant, x is time, and y is the number of remaining nuclei after a specific amount of time passes. If two decay modes exist, must use the two-term exponential model, see eq. (2.6). For each additional decay mode, you add another exponential term to the model. Examples of exponential growth include contagious diseases for which a cure is unavailable, and biological populations whose growth is uninhibited by predation, environmental factors, and so on.

2.6 Degradation Mechanism

2.6.1 Degradation Mechanism in Polycarbonate

The reactions that are produced by exposure of PC to solar light have been described by a dual photochemistry: direct phototransformation and photo-induced oxidation, with a ratio largely dependent upon the spectral distribution of the excitation light source. Excitation of PC at short wavelength involves mainly two consecutive photo-Fries rearrangements of the aromatic carbonate units leading successively to the formation of phenylsalicylate (L1) and dihydroxybenzophenone (L2) units as shown in figure 2.8. Photo-Fries products have been well defined by definite maxima in the UV and in the carbonyl range of the IR domain: L1 at 320 nm and 1689 cm^{-1} and L2 at 355 nm and 1629 cm^{-1}. As a minor pathway, L3 units are formed competitively to photo-Fries rearrangements: some radicals formed in CO–O bond scissions may decarbonylate or decarboxylate before further radical recombination or hydrogen abstraction. This leads to the formation of hydroxy-and dihydroxy-biphenyl units, aromatic ether structures and phenol as end-groups, further photolysed into a mixture of species (in a convoluted absorption) that produces the yellowing of the PC film without any defined structure (Rivaton, A. *et al.*, 2002).
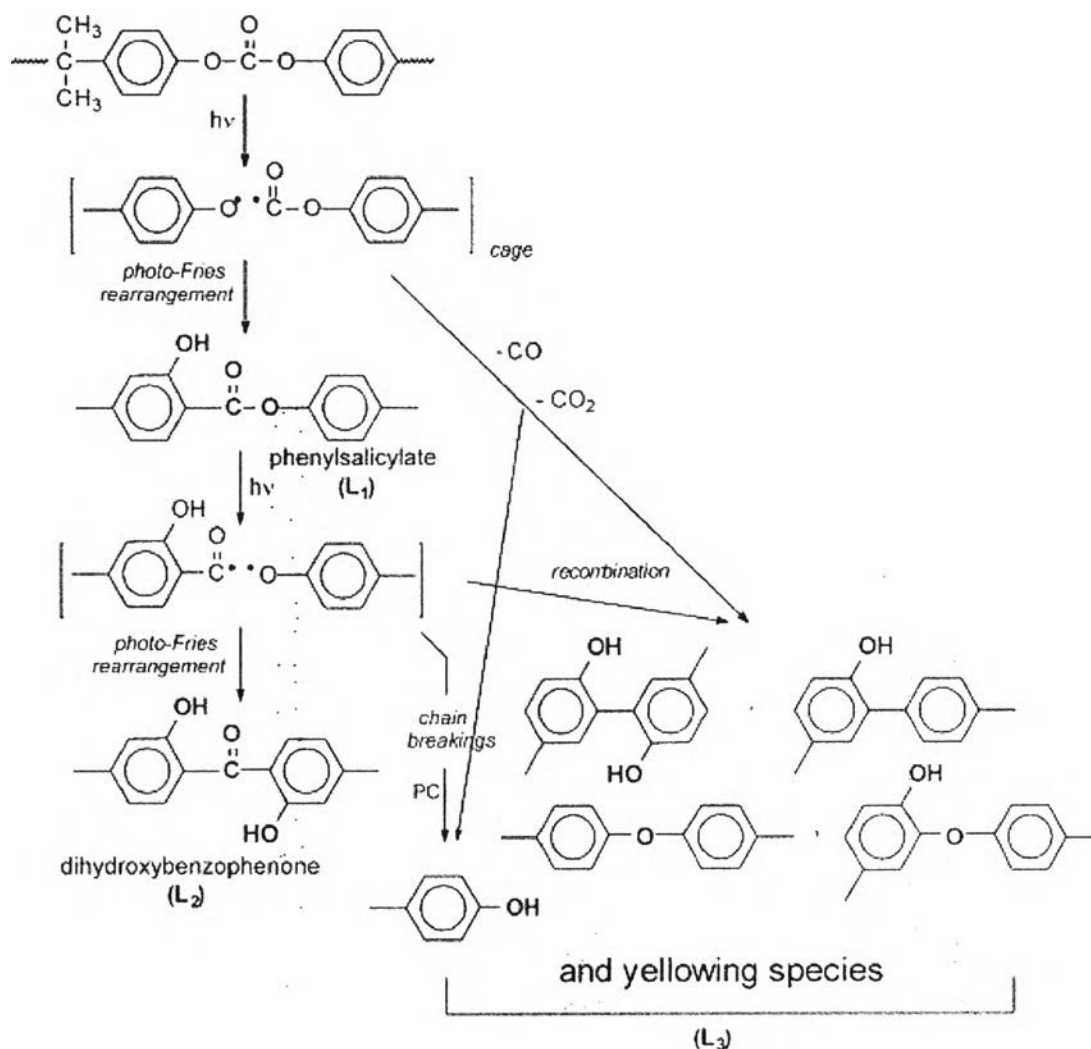
Figure 2.8 Direct phototransformation of PC at short wavelength in the absence of oxygen.

On irradiation at long wavelength (e.g. 365 nm) in the presence of oxygen, photoproducts have been shown to result mainly from the photo-induced oxidation on the gem dimethyl side-chain and from the phenyl rings oxidation. The various steps of the gem dimethyl side chain photo-oxidation, initiated by photo-Fries process, are reported in figure 2.9.
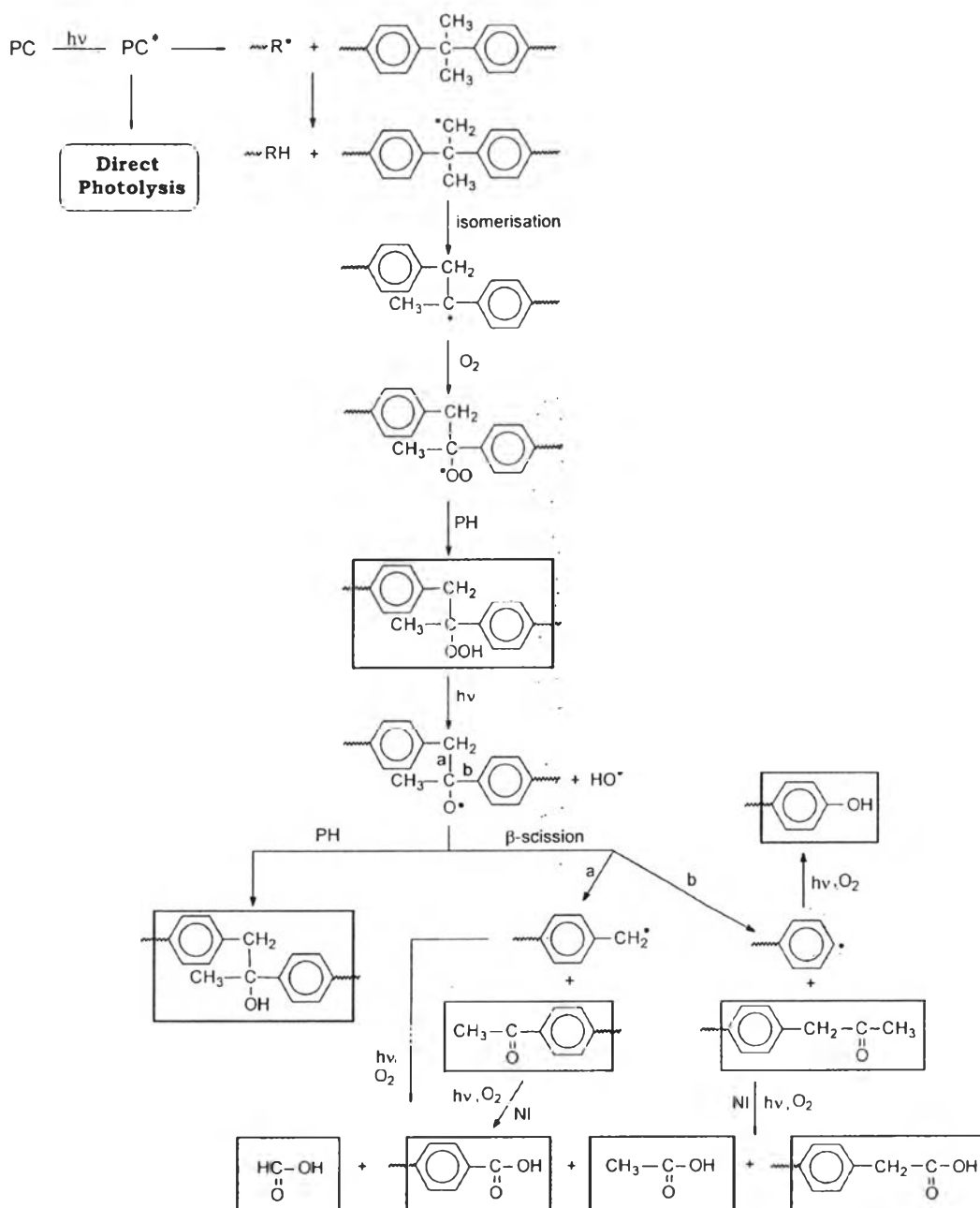
Figure 2.9 Gemdimethyl side-chain photo-oxidation of PC.

The first step of the oxidative reactions is an hydrogen abstraction on the polymeric backbone. The macroradical formed reacts with oxygen, leading to a peroxy radical that gives a hydroperoxide by abstraction of a labile hydrogen atom. Hydroperoxides decompose thermally or photochemically to give alkoxy and hydroxyl radicals (which can mainly resume the chain oxidation reaction) leading to

the formation of the various photoproducts that have been identified, namely: aliphatic (1724 cm^{-1}) and aromatic (1690 cm^{-1}) chain-ketones, aliphatic (1713 cmand aromatic (1696 cm^{-1}) chain-acids, chain-alcohols (3490 cm^{-1}), formic and acetic acid that are able to migrate in the gas phase. The opening of phenyl rings of PC has been assessed by Clark, D.T. *et al.*, 1984. It has been suggested that cyclic anhydrides (1860/1840 cm^{-1}) could be formed in the thermal transformation of dicarboxylic acidic products (1713 cm^{-1}) which appear after phenyl ring scissions under long-wavelength irrdiation (Rivaton, A.,1995). A probable mechanism of formation is reported in Scheme 3. The initiation steps by OH and ^{1}O2 have been proposed by Clark, D.T. *et al.*, 1984.
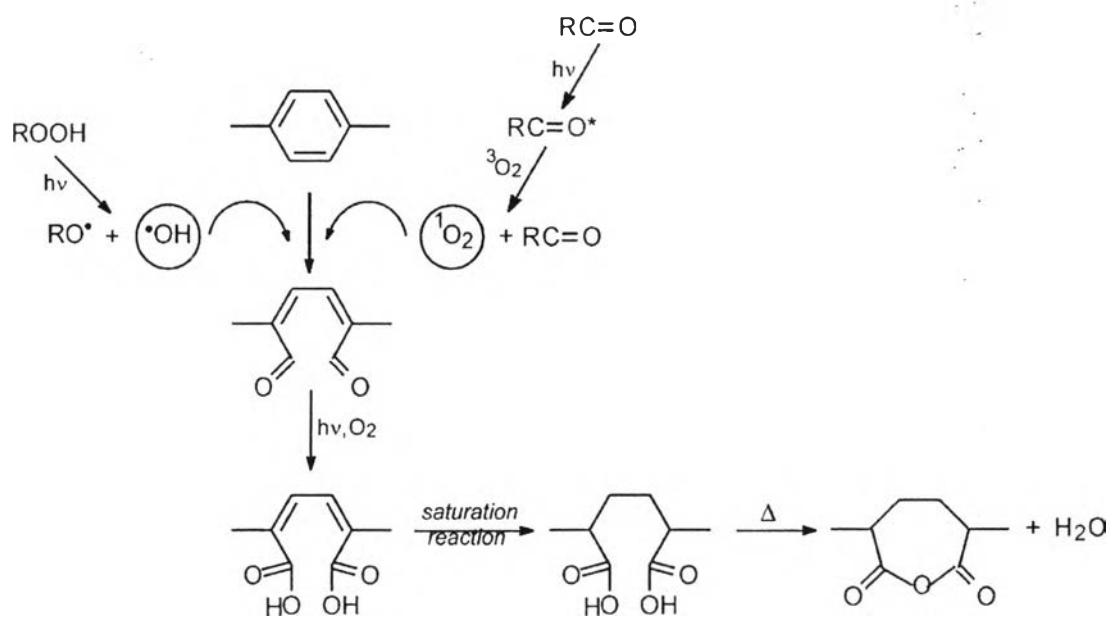
Figure 2.10 Probable mechanism of ring oxidation.