



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Ultraviolet Protection

2.1.1 Ultraviolet Radiation

Ultraviolet (UV) radiation is an electromagnetic radiation with a wavelengths in the range of 200-400 nm. The sun emits ultraviolet radiation in three regions: UVC (200-280 nm), UVB (280-315 nm) and UVA (315-400 nm). UVC, which is the most dangerous to living species, is totally absorbed by the upper layers of the atmosphere. Figure 2.1 shows the relative erythral effectiveness in UVA and UVB regions, which is a spectral dependence of the ability of UV radiation to produce erythema or an abnormal redness in human skin caused by dilation of blood vessels, the relative erythral effectiveness in 320-400 nm region is much lower than that in 280-320 (AATCC, 2004).

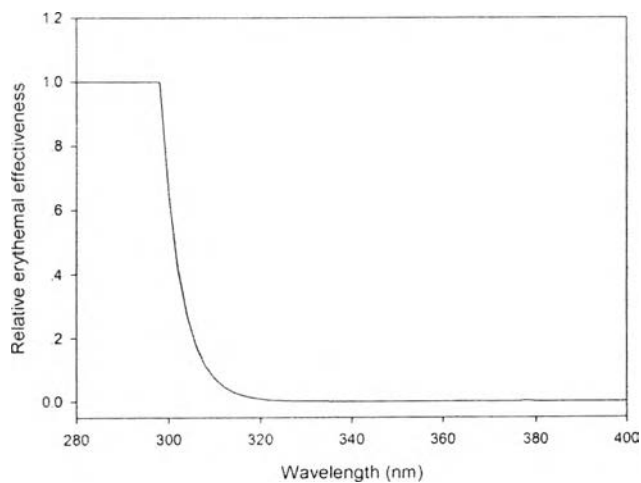


Figure 2.1 Relative erythral effectiveness in 280-400 nm region.

UVC rays have the highest energy as note above and are the most dangerous type of the ultraviolet radiation. Little attention has been given to UVC rays in the past since they are filtered out by the atmosphere. However, their use in

equipment such as pond sterilization units may pose an exposure risk, if the lamp is switched on outside of its enclosed pond sterilization unit.

UV radiation levels are reported as a solar UV-Index, developed by the World Health Organization (WHO). It has been used to report the highest level of UV radiation in any given day. The UV-Index is designed to provide the public with a numerical indication of the maximum potential solar UV radiation level during the day, the higher the number the higher the solar UV radiation hazard. The UV-Index allows for cloud cover and other environmental factors and is used worldwide for reporting UV radiation levels. UV-Index values are grouped into exposure categories of low, moderate, high, very high and extreme with corresponding color codes as shown in Table 2.1.

Table 2.1 The UV-Index exposure categories

UV-Index range	Category	Color
0-2	Low	Green
3-5	Moderate	Yellow
6-7	High	Orange
8-10	Very high	Red
≥11	Extreme	Purple

The UV spectrum has both beneficial and damaging effects on human health. A positive effect of UVB exposure is that it induces the production of vitamin D in the skin. Too little UVB radiation leads to a lack of vitamin D. An over exposure to UV radiation can result in acute and chronic health effects on the skin, eye, and immune system.

UVA, UVB and UVC can all damage collagen fibers and thereby accelerate aging of the skin. Both UVA and UVB destroy vitamin A in skin which may cause further damage. Ultraviolet radiation is a proven human carcinogen, according to the U.S. Department of Health and Human Services. UVB radiation can cause direct DNA damage. The radiation excites DNA molecules in skin cells, causing covalent bonds to form between adjacent thymine bases, producing

thymidine dimers. Thymidine dimers do not base pair normally, and this can cause distortion of the DNA helix, stalled replication, gaps, and misincorporation. These can further lead to mutations, which can result in cancerous growths. In the past UVA was considered less harmful, but today it is known that it can contribute to skin cancer via the indirect DNA damage. UVA can generate highly reactive chemical intermediates, such as hydroxyl and oxygen radicals, which in turn can damage DNA. As a defense against UV radiation, the body tans when exposed to moderate radiation depending on skin type. Within the skin is the dark pigment melanin. The purpose of melanin is to block UV-radiation and prevent damage to the skin tissues deeper down. The photochemical properties of melanin make it an excellent photoprotective agent.

Table 2.2 Comparison of sunscreens and fabrics as a protection against UV radiation (Hatch *et al.*, 2006)

Comparison factor	Comment
1. Transparency	-Sunscreens are preferred to covering the skin with fabrics.
2. Cost	-Sunscreens are consumed continuously. Fabrics labeled as UV-protective are costly but no additional cost is required for repeated use.
3. Long-lasting and photostability	-Sunscreens are temporary and must be reapplied. Fabrics keep protection over the whole day.
4. Waterproofing	-Most sunscreens must be reapplied. Fabrics do not lose the ability to protect on exposure to water.
5. Timing of application	-Sunscreens must be applied 30 minutes prior to sun exposure. Fabric may be donned at the last minute.

From American Cancer Society's 2007 Facts & Figures, more than 20 people die each day from skin cancer. Public awareness of the hazards of solar ultraviolet radiation has increased substantially in many countries. Consequently, more people have begun to take positive steps to protect themselves against ambient

UV radiation by using protective gear; hats, sunglasses, sunscreens and more importantly, clothing.

Among UV protection methods recommended by WHO, such as avoiding prolonged exposure to direct sunlight, wearing sunglasses, and using sunscreen, the use of UV-protective clothing is viewed as a positive addition. Table 2.2 shows a comparison of sunscreens and fabrics on their properties as a UV-protector.(Hatch and Osterwalder, 2006). The disadvantages of sunscreens include discomfort, the requirement for frequent reapplication, and potential hypersensitivity. Fabrics offer simple and effective, medically harmless protection against UV radiation. As a result, there is an increasing demand for clothing with UV protection.

2.1.2 UV Protective Properties of Fabric

The UV-protective properties of clothing have been known for many years and the factors that affect the amount of protection have been reported previously. Recent research work has concentrated on the effects of wetting, stretch, wear and aging on the UV protective properties of garments.

There are many factors playing a role in the amount of protection provided by fabric as listed in following: (Gie *et al.*, 1997; Alvarez and Symonowicz, 2003; Hatch and Osterwalder, 2006).

- 1) Weave: The more closely woven the fabric, the less UV is transmitted.
- 2) Color: The darker the color of the fabric, the more UV is absorbed as shown in Figure 2.2.
- 3) Weight: The thicker the fabric, the less UV is transmitted.
- 4) Water: When wet, fabrics provide less UV protection as shown in Figure 2.2.
- 5) Washing: UV protection increases after the first washing

Cotton was found to give too little sun protection (Reinert *et al.*, 1997). Davis *et al.* (1997) studied and found that all white cotton, linen, acetate, and rayon samples had an SPF (Sun Protection Factor) value of less than 15 which indicates that they do not provide sufficient protection against UV radiation.

Polyester fabrics had higher SPF values and offered higher protection than other fiber types in comparably constructed fabrics. Other works have examined directly UV protective effects of clothing on human subjects (Reinert *et al.*, 1997), and many studies have compared laboratory results based on in vitro measurements of UV protection of clothing with in vivo measurements (Stanford *et al.*, 1997; Hoffmann *et al.*, 2003; Hatch and Osterwalder, 2006).

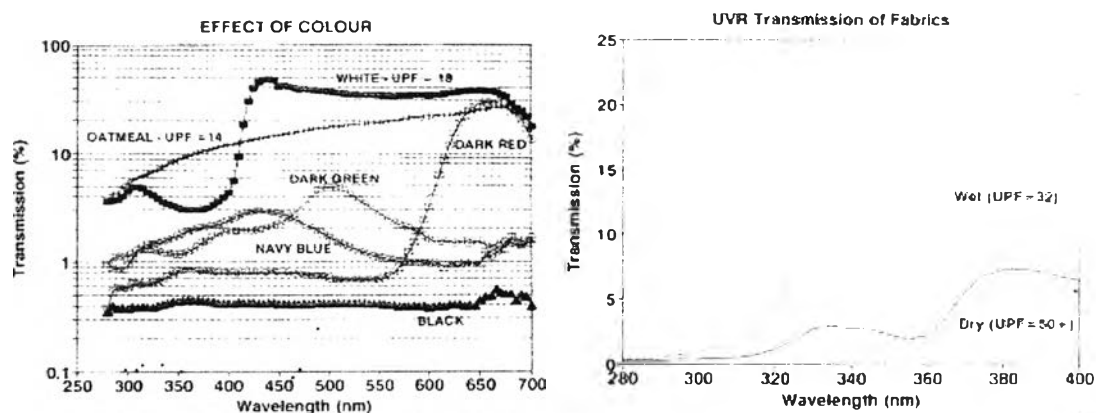


Figure 2.2 Effect of color and wetting on UV transmission of fabrics (Gie *et al.*, 1997).

There have been many studies that concentrated on the effects of dyeing, laundering, and aging on the UV protection properties of fabrics (Stanford *et al.*, 1995; Wang *et al.*, 2001; Sarkar, 2004; Gorenek and Sluga, 2004). It has been found that an increase in fabric UPF and SPF occurs after washings as a result of fabric shrinkage (Stanford *et al.*, 1995; Wang *et al.*, 2001). Dyeing fabrics reduces UV transmission and increases UPF values. Blue dye-treatment showed greater increase in UPF than yellow dye-treatment (Wang *et al.*, 2001), and an acid dyeing was more effective than an alkaline dyeing in UPF improvement (Gorenek and Sluga, 2004). A significant disadvantage is the heat retention caused by darker colored fabrics. As sun protective clothing is usually meant to be worn during warm and humid conditions, some UV-blocking textiles and clothing may be designed with ventilated weaves, and moisture wicking properties to assist in cooling and

breathability.

2.1.3 UV Absorber

In sunscreens, ingredients which absorb UVA/UVB rays, such as avobenzone and octyl methoxycinnamate, are known as absorbers. They are contrasted with physical "blockers" of UV radiation such as titanium dioxide and zinc oxide. A UV absorber is an organic or inorganic molecule which absorbs UV radiation and converts it to less harmful energy. A number of different ultraviolet absorbers exist with different absorption properties. Examples include benzotriazole, benzophenone, benzoic acid ester, and hindered amines. The followings are the Food and Drug Administration allowable active ingredients in sunscreens: p-aminobenzoic acid, avobenzone, cinoxate, dioxybenzone, octocrylene, octyl methoxycinnamate, octyl salicylate, oxybenzone, and phenylbenzimidazole sulfonic acid. The ultraviolet absorbers in sunscreens are usually aromatic molecules conjugated with carbonyl groups. This general structure allows the molecule to absorb high-energy ultraviolet rays and release the energy as lower-energy rays, thereby preventing the skin-damaging ultraviolet rays from reaching the skin. So, upon exposure to UV radiation, most of the ingredients (with the notable exception of avobenzone) do not undergo significant chemical change, allowing these ingredients to retain the UV absorbing potency without significant photo-degradation.

The photochemical mechanism of a UV absorber is a reversible process as shown in Figure 2.3. UV absorption causes the electron density to move from the phenolic oxygen and a proton transfer occurs. The isomeric form represents an excited state, which is stabilized as a result of a radiationless transition to the ground state. Thus the molecule remains chemically unchanged and is able to undergo a large number of activation-deactivation cycles (McGarry *et al.*, 1997; Paterson *et al.*, 2004).

Due to the effectiveness and the reversible reaction of the UV absorbers, a number of studies have investigated the use of UV absorbers as photostabilizer of organic compounds, for example, dyes (Wang *et al.*, 1996; Tsatsaroni and Eleftheriadis, 2004; Oda, 2005; Parejo *et al.*, 2006), and sunscreens (Chatelain *et al.*, 2001). Ultraviolet absorbers are commonly used in organic

materials such as polymers, paints, and textiles to absorb UV radiation in order to reduce the degradation (photo-oxidation) of the materials. The benzotriazole and benzophenone type UV-absorbers were found to improve light fastness of materials. (Oda, 2005; Tsatsaroni and Eleftheriadis, 2004). Wang *et al.* (1996) studied the effect of UV absorber on the photostability of dye on silk and found that addition of 2% salicylic acid benzyl ester afforded a good deal of protection against photodegradation.

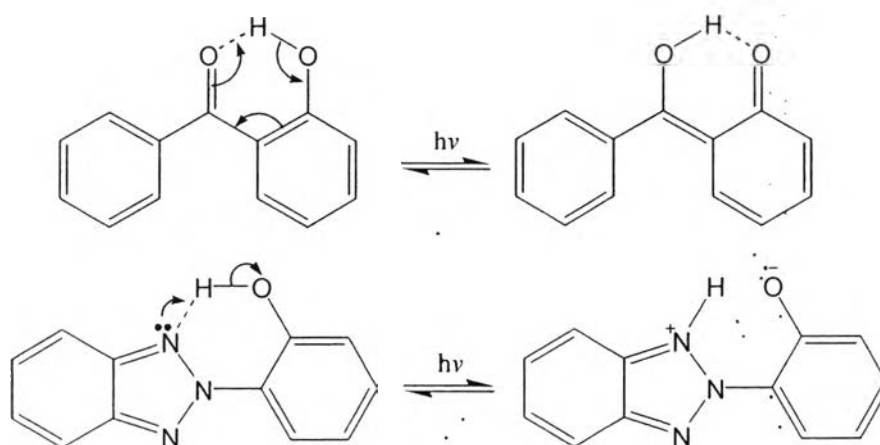


Figure 2.3 The UV absorbing mechanism of UV absorbers.

To enhance UV protection properties of fabrics, organic UV absorbers are used in a modification of the fabric. Commercial UV absorbers have been applied on cotton by the exhaustion (Abidi *et al.*, 2001) and pad-dry-cure methods (Todorova *et al.*, 2003). The resulting fabrics showed very good UV protection. Other workers have examined the use of UV absorbers in dyeing process (Reinert *et al.*, 1997), and the synthesis of dyes with a UV-absorber (Paluszkiewicz *et al.*, 2005). Paluszkiewicz *et al.* (2005) prepared dyes which included additional UV-absorber systems and applied the dyes to cotton by the pad dyeing and the exhaustion methods. The fabrics gave excellent UV protection properties, and the pad dyeing method gave a higher dyeing efficiency than the exhaustion method. In 2006, derivatives of monochlorotriazine, a colorless UV absorber, were synthesized for improvement in protective properties of cotton fabric (Czajkowski *et al.*, 2006). Scalia *et al.* (2006)

investigated the incorporation of the sunscreen agent, octyl methoxycinnamate, into cyclodextrin cavities covalently bound to cellulose fibers. From all the research reviewed, it can be concluded that organic UV absorbers have potential use in preparing UV protective clothing.

A number of research studies have investigated the use of inorganic UV absorbers and hybrid organic/inorganic coating to improve UV protection of fabrics. Inorganic UV absorbers like TiO_2 and ZnO absorb radiation with an energy higher than their bandgap energy; e.g. $E_{\text{gap}/\text{TiO}_2} = 3.0 \text{ eV}$ and $E_{\text{gap}/\text{ZnO}} = 3.2 \text{ eV}$ (Czajkowski *et al.*, 2006). This bandgap energy depends strongly on the kind and degree of crystallinity of the inorganic coating. These compounds can be applied as pigments in a binder or can be deposited as pure oxide layer from liquid phase.

In 2000 Hoffmann *et al.* treated viscose summer fabrics by depositing a pigment titanium dioxide in the viscose yarn and found that the treated garments had higher UPF. Xin *et al.* (2004, 2005) developed the sol-gel method to form a thin layer of titania on cotton fibers and the treated fabric showed much improved protection against UV radiation. The dumbbell-shaped ZnO microcrystallites were synthesized and coated on cotton, and it was found that its unique morphology affected the UV-blocking property of the fabric (Wang *et al.*, 2005). Mahltig *et al.* (2005) used sol-gel technique to prepare coating from TiO_2 combined with embedded organic UV absorbers, and the UV transmission was significantly reduced. In 2006, a ZnO -polystyrene nanohybrid coating on cotton was successfully prepared by in-situ polymerization method in miniemulsion (Lu *et al.*, 2006). The treated fabrics provided ultrahigh UV protection. During the same time, a ZnO/TiO_2 nanoparticle-embedded acrylic film coating on Kevlar was reported by Katangur *et al.* (2006). These methods gave an excellent UV protection but the process of these techniques are not convenient. Moreover, the wash fastness of some techniques was limited.

2.1.4 Ultraviolet Protection Rating

UV protective clothing is specifically designed for UV protection and the fabric can be rated for its level of UV protection using a standardized method. Quantifying the protection provided by clothing against solar UV radiation has

resulted in the development of standard test methods for determining UV protection. The first of these was issued in Australia and New Zealand in 1996 as AS/NZS 4399.

A relatively new rating designation for UV protective textiles and clothing is UPF (Ultraviolet Protection Factor). Developed in 1998, the testing standard for UV protective fabrics in the United States is the American Association of Textile Chemists and Colorists (AATCC) Test Method 183.

Ultraviolet protection properties of fabrics can be presented as the percent UV blocking and the UPF value. According to AATCC Test Method 183-2004, the average A-range ultraviolet (UV-A) transmittance and the average B-range ultraviolet (UV-B) transmittance can be calculated using Equations 2.1 and 2.2, respectively.

$$T(UV - A)_{AV} = \frac{\sum_{315nm}^{400nm} T_{\lambda} \times \Delta\lambda}{\sum_{315nm}^{400nm} \Delta\lambda} \quad (2.1)$$

$$T(UV - B)_{AV} = \frac{\sum_{280nm}^{315nm} T_{\lambda} \times \Delta\lambda}{\sum_{280nm}^{315nm} \Delta\lambda} \quad (2.2)$$

The percent blocking for UV-A and for UV-B are subsequently calculated using Equations 2.3 and 2.4.

$$\% UV - B \text{ blocking} = 100\% - T(UV - B) \quad (2.3)$$

$$\% UV - A \text{ blocking} = 100\% - T(UV - A) \quad (2.4)$$

Ultraviolet Protection Factor (UPF) is the scientific term used to indicate the amount of UV protection provided to skin by fabric. AATCC 183 method defines the UPF rating for a fabric/textile as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the test fabric. For example, a fabric with a UPF of 30 means that if 30 units of UV radiation fall on the fabric, only 1 unit will pass through. In this standard, a UV protection factor (UPF) is determined by the

measured transmission with the spectral irradiance and the erythemal sensitivity as shown in Equation 2.5:

$$UPF = \frac{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda} \quad (2.5)$$

where:

E_{λ} = relative erythemal spectral effectiveness

S_{λ} = solar spectral irradiance in $\text{W m}^{-2} \text{nm}^{-1}$

T_{λ} = average spectral transmittance of fabric

$\Delta\lambda$ = measured wavelength interval in nm

λ = wavelength in nm

The calculated UPF value indicates how much longer a person can stay in the sun when fabric covers the skin as compared with the length of time in the sun without fabric covering to obtain the same erythemal response. According to AS/NZS 4399: 1996, fabrics can be classified according to their UPF values as shown in Table 2.3.

Table 2.3 Classification of UV protection level of fabrics

UPF	Protection level
15-24	Good
25-39	Very good
≥ 40	Excellent

AATCC 183 should be used in conjunction with other related standards including American Society for Testing and Materials (ASTM) D 6544 and ASTM D 6603. ASTM D 6544 specifies simulating the life cycle of a fabric so that a UPF test can be done at the end of a fabric's life cycle. ASTM D 6603 is a consumer

format recommended for visible hangtag and care labelling of sun protective clothing and textiles. A manufacturer may publish a test result to a maximum of UPF 50+.

2.2 Admicellar Polymerization

Admicelle is the term used to refer to a bilayer of surfactant molecules adsorbed on a solid surface. Under suitable conditions, an ionic surfactant will normally form aggregates at the hydrophilic surfaces of a substrate in aqueous solution. To minimize the free energy, the surfactant molecules will tend to form bilayer with the hydrophilic head groups of the upper-layer molecules facing the aqueous water and their hydrophobic tails interacting with the hydrophobic tails of the lower-level surfactant molecules forming a hydrophobic core in the admicelle.

The technique of ultrathin polymer film formation by the use of surfactant adsorption from aqueous solution onto a solid surface in the form of admicelles was first reported in the 1980s. Wu *et al.* (1987) first investigated this novel approach for the formation of polystyrene from styrene adsolubilized in sodium dodecyl sulfate bilayers on alumina.

Admicellar polymerization is an *in-situ* polymerization reaction in the core of the surfactant bilayer adsorbed on the substrate surface to apply thin polymeric film on the substrate surface. There are three main steps in the admicellar polymerization process as shown in Figure 2.4, surfactant adsorption to form a bilayer on the substrate surface called the admicelle formation step, monomer adsolubilization into the admicelle called the monomer adsolubilization step, and polymerization of the monomer in the admicelle called the *in-situ* polymerization step.

The first step is admicelle formation. Figure 2.5 shows a typical adsorption isotherm for an ionic surfactant onto an oppositely charged substrate (Rosen, 2004). The isotherm can be divided into four regions. In Region I, the adsorption increases slowly with increasing surfactant concentration with the surfactant adsorbed as isolated molecules on the solid surface. In Region II, there is a sharp increase in the slope of the isotherm due to cooperative adsorption and the formation of surfactant aggregates. In Region III, there is a reduction in the slope of the isotherm indicating

that the surface is near saturation. In Region IV, as the concentration reaches the critical micelle concentration (CMC), excess surfactant forms micelles in solution and the adsorption becomes constant.

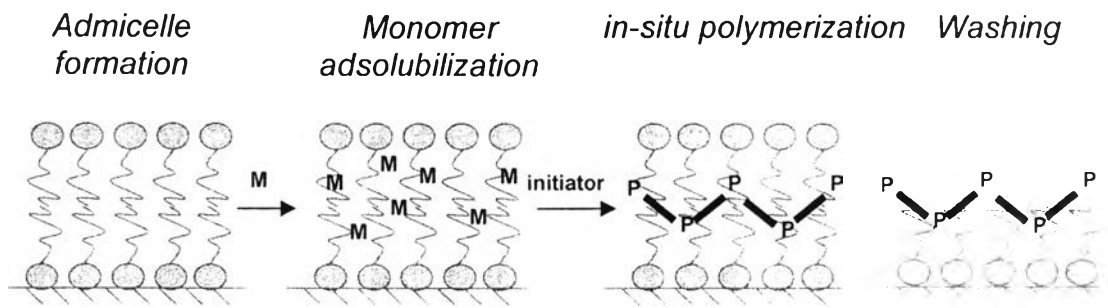


Figure 2.4 The steps in the admicellar polymerization process.

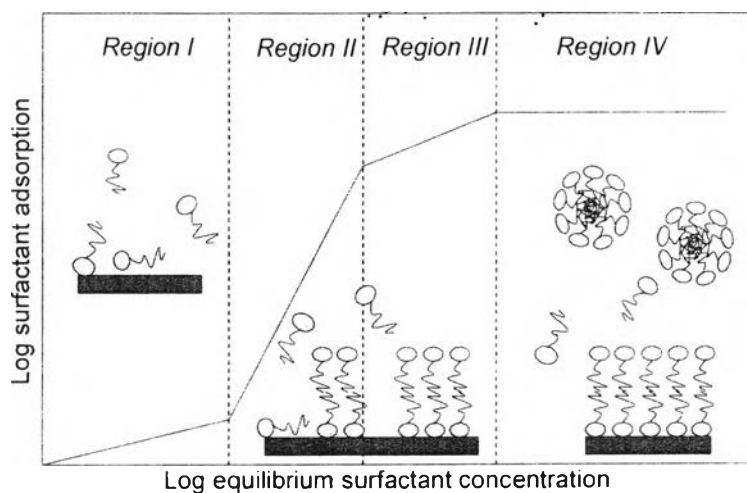


Figure 2.5 Typical adsorption isotherm of an ionic surfactant on an oppositely charged substrate

In the monomer adsolubilization step, the hydrophobic monomer molecules preferentially partition into the hydrophobic interior of the admicelle since the surfactant concentration used is below the CMC. In the third step, an initiator is introduced into the solution and polymerization is accomplished. During the polymerization, the admicelle serves as the primary loci for the in-situ

polymerization, with very little of the reaction occurring in the bulk solution. After the polymerization reaction is complete, the upper-layer surfactant is removed by washing with water to expose the polymer film on the substrate surface.

After Wu *et al.*, (1987) succeeded in the formation of polystyrene on alumina, many works have been carried out on the use of adsorbed surfactant assemblies as a medium for formation of thin polymer film on solid substrates. Thin film of polypyrrole was successfully formed on alumina surfaces using admicellar polymerization technique (Funkhouser *et al.*, 1995). and on mica and graphite using admicellar polymerization under conditions of depleting adsolubilization (Yuan *et al.*, 2002). In the latter case, the general morphology of polypyrrole film consisted of small islands connected with small disks in a weblike pattern. Besides, polymerization in the absence of surfactant was investigated and it was found that there was a poor control of the amount of pyrrole adsorbed.

Many works have also been done on the use of admicellar polymerization to modify the wetting behavior of solid substrates. Poly(methyl methacrylate) and polystyrene thin films were deposited onto aluminium substrates using the admicellar polymerization technique, making the substrates exhibit hydrophobic behavior with better corrosion protection (Matarredona *et al.*, 2003). With the same objective of inhibiting corrosion in aluminium, a thin film of poly(2,2,2-trifluoroethyl acrylate) or PTFEA was deposited on aluminium alloy substrates (Le *et al.*, 2004). It was found that PTFEA was more hydrophobic and exhibited better corrosion protection than poly(methyl methacrylate) film. In addition, surface characterization showed that the polymeric film was approximately 10 nm thick. The use of admicellar polymerization to improve properties of inorganic fillers in tires was explored by O'Haver (1994). Barraza *et al.* (2001) investigated admicellar polymerization of styrene-isoprene copolymer on glass fibers in order to improve interfacial adhesion in composites.

More recently, the admicellar polymerization process has been used to form thin polymeric film on a textile surface to modify its properties. Compared to pad-dry-cure, the conventional method for applying finishing agent to fabrics, admicellar polymerization is simple with low energy consumption, and the applied film is very thin, so the fabric still retains its pliability and soft touch. In 2002 Pongprayoon *et al.*

prepared hydrophobic cotton by formation of polystyrene film on the cotton surface via admicellar polymerization technique. Methachan *et al.* (2002) showed that good air permeability of the fabric was maintained indicating that there was no blocking of the interstices between fibers and yarns in admicellar polymerization. Low-resistivity fabric was prepared by forming a thin layer of conductive polymers (polypyrrole, polyaniline, and polythiophene) on cotton and polyester fabrics (Lekpittaya *et al.*, 2004). By hydrolyzation of poly(methyl methacrylate) film formed via admicellar polymerization, hydrophilic polyester fabric was successfully prepared (Siriviriyanun *et al.*, 2006). Antimicrobial cotton was prepared recently via admicellar polymerization using *N*-halamine biocidal monomer (Ren *et al.*, 2008).

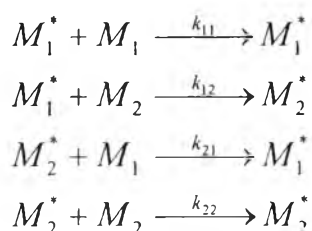
2.3 Copolymerization and Monomer Reactivity Ratio

A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species. Copolymerization is very important from the technological viewpoint. It greatly increases the ability of the polymer scientist to tailor-make a polymer product with specific desired properties. Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two (or more) monomer units in the copolymer products. Examples of commercially relevant copolymers include acrylonitrile-butadiene-styrene rubber, styrene-acrylonitrile, styrene-isoprene-styrene and ethylene-vinyl acetate.

Since a copolymer consists of at least two types of constitutional units, copolymers can be classified based on how these units are arranged along the chain. These include: alternating copolymers with regular alternating A and B units, random copolymers with random sequences of monomers A and B, statistical copolymers in which the ordering of the distinct monomers within the polymer sequence obeys known statistical rules, and block copolymers comprising of long sequences of each monomer in the copolymer chain. Block copolymers with two or three distinct blocks are called diblock and triblock copolymers, respectively (Odian, 1991).

It is well-known that copolymerization is an effective approach to obtain materials with tailored properties that are usually improved with respect to those of the homopolymers. Depending on the utilized monomers, properties of copolymer can be easily varied. In some applications the differences in the radiation emission or absorption of each monomer are being utilized. Recently, copolymerization has been used in the preparation of electroluminescent polymers with the aim of producing easy tuning of emission colors or adjustable light emission (Cho *et al.*, 1999; Sohn *et al.*, 2002; Peng *et al.*, 2006). The method has also been employed to improve the performance of polymers containing photochromic functional groups, such that the final copolymer will possess photochromophores with uniform distribution (Buchholtz *et al.*, 1993; Liang *et al.*, 2005). Balaji *et al.*, (2004) synthesized photoresponsive copolymers containing pendant chlorocinnamoyl moieties and found that the photosensitivity depended on copolymer composition. It was suggested that the copolymers in the whole range of compositions might be useful for different types of applications. In the present work copolymerization was utilized to achieve a broader and more uniform UV absorbance over the entire UV region to improve the performance of UV-protective clothing.

The composition of a copolymer is usually different from the composition of the comonomer feed. Determination of the copolymerization composition has been studied by assuming that the chemical reactivity of the propagating chain in a copolymerization is dependent on the chain composition preceding the last monomer unit. This is referred to as the first-order Markov or terminal model of copolymerization. Copolymerization of the two monomers, M_1 and M_2 , leads to two types of propagating species represented by M_1^* and M_2^* . Based on the assumption above, four propagation reactions are then possible.



where k_{mn} is the rate constant for a propagating chain ending in M_m adding to monomer M_n . The rates of disappearance of the two monomers are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \quad (2.6)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \quad (2.7)$$

Dividing Equation 2.6 by Equation 2.7 yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \quad (2.8)$$

A steady state concentration is assumed for each of the reactive species, the rates of interconversion are equal,

$$k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1] \quad (2.9)$$

Combining the result with the parameters r_1 and r_2 defined by

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (2.10)$$

one finally obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} \quad (2.11)$$

Equation 2.11 is known as the copolymerization equation or the copolymer composition equation. The copolymer composition; $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units in the copolymer. The parameters r_1 and r_2 are termed the monomer reactivity ratios. The tendency of two monomers to copolymerize is noted by r values. An r_1 value greater than unity means that M_1^* preferentially adds M_1 instead of M_2 , while an r_1 value less than unity means that M_1^* preferentially adds M_2 . At $r_1 r_2 = 1$, an ideal copolymerization occurs where the two types of propagating chains show the same preference for adding one or the other monomer. When $r_1 = r_2 = 0$, the two types of propagating chains preferentially add the other monomer and the copolymerization is referred to as an alternating copolymerization. As $r_1 r_2$ product decreases from unity toward zero, there is an increasing tendency toward alternation. If both r_1 and r_2 are greater than unity, there is a tendency to form a block copolymer (Odián, 1991).

Among the kinetic parameters in copolymerization, the reactivity ratios give a clear idea of the average composition and the monomer sequence distribution in a

copolymer system. The standard method involves the preparation and isolation of a series of copolymers with molar compositions covering all the range from 0-1. Spectroscopic methods have been developed to estimate the copolymer composition, such as NMR (Gan *et al.*, 1994; Aguilar *et al.*, 2002) and FTIR (Mao *et al.*, 1993, 1995). From the copolymer composition data, various methods have been used to obtain monomer reactivity ratios. The most frequently used methods involve a rearrangement of the copolymer composition equation into a linear form.

Mayo and Lewis (1944) rearranged Equation 2.11 into

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{d[M_2]}{d[M_1]} \left\{ 1 + \frac{r_1[M_1]}{[M_2]} \right\} - 1 \right] \quad (2.12)$$

Data for the feed and copolymer compositions for each experiment with a given feed are substituted in to Equation 2.12 and r_2 is plotted as a function of various assumed values, of r_1 . Each experiment yields a straight line and the intersection of the lines for different feeds gives the best values of r_1 and r_2 .

Fineman and Ross (1950) rearranged the equation to

$$G = r_1 F - r_2 \quad (2.13)$$

where $G = X(Y-1)/Y$, $F = X^2/Y$, $X = [M_1]/[M_2]$, and $Y = d[M_1]/d[M_2]$. G is plotted against F to yield a straight line with slope r_1 and intercept r_2 .

Kelen and Tudos (1975) refined the linearization method by introducing an arbitrary positive constant α into Equation 2.13 to spread the data more evenly so as to give equal weighting to all data points. Their results are expressed in the form

$$\eta = \left[r_1 + \frac{r_2}{\alpha} \right] \varepsilon - \frac{r_2}{\alpha} \quad (2.14)$$

where $\eta = G/(\alpha + F)$, $\varepsilon = F/(\alpha + F)$ and $\alpha = (F_{min}F_{max})^{1/2}$. Plotting η against ε gives a straight line that yields $-r_2/\alpha$ and r_1 as intercepts on extrapolation to $\varepsilon = 0$ and $\varepsilon = 1$, respectively.

FTIR is one of the widely used methods for analysis of copolymers and the determination of reactivity ratios because the analysis can be performed quickly and at low cost. Şolpan *et al.* (1996) used FTIR for quantitative determination of unreacted monomers and calculated copolymer composition. The results agreed very well with that from elemental analysis of the copolymer. The reactivity ratios

calculated from FTIR spectra of the copolymer also agreed with the elemental analysis (Pekel *et al.*, 2001). Canto *et al.* (2002) determined the composition of styrene-glycidyl methacrylate copolymer using an FTIR calibration curve based on prepared mixtures of two monomers at known compositions. The results were in good agreement with a titration method. Thus it can be concluded that FTIR can provide not only qualitative but also very good quantitative analysis of copolymers.

2.4 Silane Coupling Agents

Silane coupling agents have been widely employed for surface modifications. They are often used to improve the adhesion between a polymer matrix and reinforcements in a composite. The general formula of organofunctional silanes is $YRSiX_3$ where X and Y represent a hydrolyzable and an organofunctional groups, respectively. The organofunctional groups are chosen for reactivity or compatibility with the polymer while the hydrolyzable groups are merely intermediates in the formation of silanol groups for bonding to mineral surfaces (Plueddemann, 1982).

Trialkoxysilanes, $RSi(OR)_3$, hydrolyze stepwise in water to give the corresponding silanols, which condense to siloxanes. The reactions are shown in Figure 2.6. The hydrolysis is relative fast while the condensation reaction is much slower. Silanol groups are necessary for silanes to function as coupling agents between organic resins and mineral fillers.

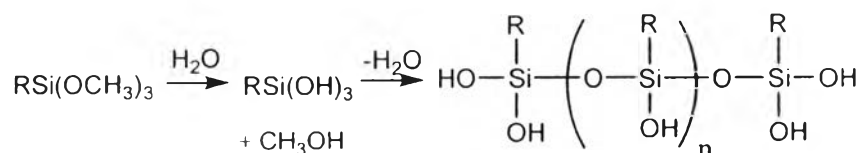


Figure 2.6 Hydrolysis and condensation of trialkoxysilanes.

Some representative organofunctional silanes available in commercial quantities are shown in Table 2.4.

Table 2.4 Representative commercial silanes (Plueddemann, 1982)

Organofunctional group	Chemical Structure
1. Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$
2. Chloropropyl	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
3. Epoxy	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$
4. Methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$
5. Primary amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
6. Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
7. Mercapto	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$

Vinyl silane, also called ethenyl silane, is an organic chemical with chemical formula $\text{C}_2\text{H}_6\text{Si}$, or $\text{CH}_2=\text{CH}-\text{SiH}_3$. Vinyl silane is used as a monomer for some copolymer plastics such as ethylene-vinyl silane and ethylene-vinyl acetate-vinyl silane. It is also used as a cross-linking agent during the manufacture of cross-linked polyethylene. Vinyl silane is also used as a coupling agent for treatment of glass fibers in order to form stronger bonds with resin and produce fiberglass with better mechanical properties. The silane group attaches to the glass substrate via covalent Si-O-Si bond, while the resin reacts with the vinyl group and binds to it. Moreover, vinyl silanes can copolymerize readily with vinyl esters, vinyl chloride and allyl ester. Vinyl silane copolymers are generally of rather low molecular weight (Plueddemann, 1982).

Vinyltriethoxysilane (VTES), which is relatively inexpensive silane, has been used to modify glass surface to improve its scratch protection (Prikryl *et al.*, 2005), and to functionalize mesoporous silica (Chong *et al.*, 2004). Li *et al.* (2006) investigated VTES sol-gel and its coating on aluminum using Infrared and Raman spectroscopy. The anticorrosion and hydrophobic properties of the coated aluminum were found to significantly increase.

Recently, silane coupling agents containing polymerizable groups have been used to modify substrates, which were subsequently grafted by polymerization. To enhance the interfacial adhesion in nanocomposites, alumina was treated with 3-methacryloxypropyl trimethoxysilane followed by grafting polymerization of polystyrene and polyacrylamide (Rong *et al.*, 2002). Tang *et al.* (2006) did powder coating of TiO₂ by using 3-methacryloxypropyl trimethoxysilane followed by minisuspension polymerization of polyacrylate. The 3-methacryloxypropyl trimethoxysilane-treated TiO₂ was also studied by Chen *et al.* (2006). The double bonds on the surface were subsequently copolymerized with methyl methacrylate and butyl acrylate. Cech *et al.* (2006) studied plasma-polymerized and polycondensed thin films of VTES on glass substrates employed as reinforcements in plastics. They showed that the double bond in the vinyl group was split during the plasma process even if a very low density was used and the thickness of plasma polymer films could be easily varied in a range of 15 nm-2 μm with the film surface relatively flat. Jia *et al.* (2007) prepared nanocomposites of poly(vinyl alcohol)/silica nanoparticles by radical copolymerization of vinyl acetate and vinyl silica nanoparticles functionalized by VTES. The treated substrates such as glass fibers, alumina, silica, and TiO₂ are mostly used as reinforcements in polymer composites or nanocomposites. However, there has been no study on the use of this technique to modify a textile fabric.

Silane adsorption on cellulose fibers through the hydrolysis and condensation reactions was studied by ¹H, ¹³C and ²⁹Si NMR (Salon *et al.*, 2005). The rate of hydrolysis depended on the type of silanes and the adsorption isotherm suggested that silane adsorption proceeded through a monolayer formation, followed by multilayer mechanism. Dubitsky *et al.* (2005) studied the hydrolysis of VTES and found that under neutral conditions, the hydrolysis of VTES in acetonitrile is very slow, but, in the presence of even a very small amount of acid, the rate increased dramatically. The prehydrolyzed silane can adsorb readily on the surface of cellulose but a simple extraction with ethanol can remove these molecules. Only a heat treatment can induce a condensation between the OH-groups of the hydrolyzed silanes and those present at the surface of cellulose (Abdelmouleh *et al.*, 2002). The interaction between silanes and a substrate was found to be covalent bonding (Gent

and Hsu, 1974; Abdelmouleh *et al.*, 2002), and the solid-state ^{13}C NMR showed covalent bond formation between vinyl silane and polymer (Fyfe and Niu, 1995).

From the literature reviews, a cellulose fiber with hydroxyl groups can react with VTES, through its hydrolyzed ethoxy groups, followed by polymerization of the vinyl group with a suitable comonomer to obtain the desired properties. In this process the ethoxy groups in VTES are first hydrolyzed to silanol groups which then formed hydrogen bonding with the hydroxyl groups of the cellulose molecules on the cotton surface. The condensation reaction occurs when the fabric is dried leading to covalent bonding between the silane and cotton. After this, the vinyl groups of VTES are allowed to undergo polymerization reaction with a suitable monomer to form a polymer film coated on the fiber surface.