อิทธิพลของสารเสริมเสถียรภาพต่อรังสียูวีต่อการเสื่อมสภาพทางแสงของสารประกอบ พอลิไวนิลคลอไรด์ผงไม้และพอลิไวนิลคลอไรด์ซังข้าวโพดโดยการทดสอบ การทนต่อสภาพดินฟ้าอากาศทางธรรมชาติ

นา<mark>งสาววัลยา</mark> วงษาหาร

## ศูนย์วิทยทรัพยากร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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## INFLUENCE OF UV STABILIZERS ON PHOTO-DEGRADATION OF PVC/WOOD FLOUR AND PVC/CORNCOB COMPOSITES BY NATURAL WEATHERING TEST

Miss Wanlaya Wongsaharn

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering Program in Chemical Engineering Department of Chemical Engineering Faculty of Engineering Chulalongkorn University Academic Year 2008

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Thesis Title	INFLUENCE OF UV STABILIZERS ON PHOTO-
	DEGRADATION OF PVC/WOOD FLOUR AND
	PVC/CORNCOB COMPOSITES BY NATURAL
	WEATHERING TEST
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วัลยา วงษาหาร: อิทธิพลของสารเสริมเสถียรภาพต่อรังสียูวีต่อการเสื่อมสภาพทางแสง ของสารประกอบพอลิไวนิลคลอไรด์ผงไม้และพอลิไวนิลคลอไรด์ขังข้าวโพดโดยการ ทดสอบการทนต่อสภาพดินฟ้าอากาศทางธรรมชาติ (INFLUENCE OF UV STABILIZERS ON PHOTO-DEGRADATION OF PVC/WOOD FLOUR AND PVC/CORNCOB COMPOSITES BY NATURAL WEATHERING TEST) อ. ที่ปรึกษา วิทยานิพนธ์หลัก : อ.ดร.อนงค์นาฏ สมหวังธนโรจน์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ. ดร. ศราวุธ ริมดุสิต, 92 หน้า.

วัสดุประกอบแต่งทดแทนไม้ที่ต้องสัมผัสกับแสงแดดเป็นเวลานาน จะนำไปสู่การ เสื่อมสภาพเนื่องจากแสงแดด ดังนั้นจึงมีความจำเป็นอย่างยิ่งที่จะต้องพัฒนาความทนทานของ ผลิตภัณฑ์โดยเติมสารเสริมเสถียรภาพต่อรังสียูวีลงไปในวัสดุประกอบแต่งทดแทนไม้ ในงานวิจัยนี้ ใช้พอลิไวนิลคลอไรด์เป็นเมตริกซ์ และใช้สารตัวเติมสองชนิดคือ ไม้ลักและขังข้าวโพดที่มีขนาด อนุภาค 250-425 ไมโครเมตร และใช้ในปริมาณ 60 phr สารเสริมเสถียรภาพต่อรังสียุวีที่เลือกใช้ ในการศึกษานี้เป็นเกรดทางการค้าทั้งสองชนิดและเป็นชนิดที่ดูดซับรังสียูวี ชิ้นงานตัวอย่างในการ ทดลองจะถูกนำไปตากแดดเป็นเวลา 4 เดือน และนำมาทดสอบการเปลี่ยนแปลงของสี และ ทดสอบคุณสมบัติเชิงกลทุกสัปดาห์และทุกเดือนตามลำดับ โดยการทดสอบการทนต่อสภาพดิน ฟ้าอากาศทางธรรมชาติ จากผลการทดลองแสดงให้เห็นว่า สารเสริมเสถียรภาพต่อรังสียวีสามารถ ยึดเวลาการเปลี่ยนแปลงของการขีดจาง และการเปลี่ยนแปลงของสีของพอลิไวนิลคลอไรด์ไม่ใส่ สารเติม แต่ไม่มีผลต่อสารประกอบแต่งพอลิไวนิลคลอไรด์ นอกจากนี้หลังการทดสอบการทนต่อ สภาพดินฟ้าอากาศสารประกอบแต่งพอลิไวนิลคลอไรด์ผงไม้สัก มีการเปลี่ยนแปลงการขีดจางเพิ่ม มากขึ้นกว่าสารประกอบแต่งพอลิไวนิลคลอไรด์ขังข้าวโพด ยิ่งไปกว่านั้นสารเสริมเสถียรภาพต่อ รังสียูวียังสามารถลดการสูญเสียคุณสมบัติด้านการดึงยึด และคุณสมบัติด้านการดัดโค้งของพอลิ ไวนิลคลอไรด์ไม่ใส่สารเติมและสารประกอบแต่งพอลิไวนิลคลอไรด์ ส่วนชนิดและปริมาณสารเสริม เสถียรภาพต่อรังสียูวี ไม่ส่งผลต่อการเปลี่ยนแปลงการขีดจาง การสูญเสียคุณสมบัติด้านการดึงยึด และการดัดโค้ง

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> WANLAYA WONGSAHARN : INFLUENCE OF UV STABILIZERS ON PHOTO-DEGRADATION OF PVC/WOOD FLOUR AND PVC/CORNCOB COMPOSITES BY NATURAL WEATHERING TEST. THESIS PRINCIPAL ADVISOR: ANONGNAT SOMWANGTHANAROJ, Ph.D., THESIS COADVISOR : ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., 92 pp.

Long-term exposure to sunlight of wood plastic composites (WPCs) leads to photo-degradation. Therefore, it is essential to develop the durability of products by adding UV stabilizers into WPCs. In this research, polyvinyl chloride (PVC) is a matrix and two types of fillers, which are teak wood and corncob with particle sizes 250-425 µm and a fixed content of 60 phr, were used. UV stabilizers used in this study were two types of commercial grade UV absorber. The samples were exposed to sunlight for 4 months. The color change and mechanical properties of samples were determined every week and every month, respectively by natural weathering test method. The results showed that UV stabilizers can delay the lightness change and the color change of PVC but did not significantly affect on PVC/composites. In addition, the lightness of PVC/teak wood flour (PVC/TWF) composites changed more than that of PVC/corncob (PVC/CC) composites after weathering test. Moreover, UV stabilizer can delay the loss in flexural and tensile properties of PVC and PVC composites. The type and loading of UV stabilizer had no significantly affect on the lightness change, flexural and tensile property loss.

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#### **CHAPTER I**

#### **INTRODUCTIONS**

#### **1.1 General Introduction**

In recent years, wood plastic composites (WPCs) have grown rapidly because these composites are less expensive but show better mechanical properties (e.g. higher stiffness) than pure plastics [12]. The use of wood composites in many applications e.g. roofs, deck boards, door and window profiles offer makes them expose to outdoor environments; therefore, degradation occurs. Four major factors of environmental degradation are ultraviolet (UV) radiations, atmospheric oxygen, moisture and pollutants [11]. Long-term exposure to sunlight leads to the photo-degradation of polymers, which, results in breaking down the polymer chains, cracking of surface, change in color and mechanical properties loss. Polymers containing aromatic or carbonyl groups in their repeating unit are likely to absorb the terrestrial sunlight (wavelength  $\lambda$ >290 nm) and usually become photosensitive materials. Polyvinyl chloride (PVC) is an important commercial polymer, which exhibits the highest sensitivity toward UV radiation. Because of various chemical reactions occurring upon exposure to UV radiation, PVC undergoes significant changes of its physical and mechanical characteristics [19].

Wood and natural polymer are also degraded by sunlight. Weathering of this material is caused by the UV radiation portion of sunlight. The UV radiation has sufficient energy to chemically degrade wood structural component (lignin and carbohydrates). Especially, wood exposed outdoors will undergo a rather rapid color change [21].

Laurent M. et al [11] investigated the color changes of neat rigid PVC and rigid PVC/wood-fiber composites, by performing before and after accelerated UV-weathering tests. The results indicated that the color of the composites changed more obviously than that of neat PVC. Titanium dioxide (TiO<sub>2</sub>) has been proved to be able

to protect against color changes of PVC/wood-fiber after accelerated UV-weathering. For example, Nicole, M. and Laurent, M. [18] reported that the HDPE/wood flour composites, which were exposed to UV radiation with water spray, showed greater discoloration and more flexural and strength loss than those exposed to UV radiation alone. Nicole, M. and Laurent, M. also reported that the HDPE/wood flour composites with colorant and 2-(2H-benzotriazole-2-yl)-4,6-ditertpentylphenol as a UV absorber (UVA) showed smaller color change than that with hindered amine light stabilizer (LS1 and LS2) after weathering test.

Therefore, to limit or to postpone the onset of environmental degradation, several types of UV stabilizers can be added to polymer. Commercial grades of UV stabilizers which are available are benzophenones, benzotriazoles, small dispersed particles such as carbon black,  $TiO_2$  and inorganic pigments. Other effective UV stabilizers are UV quenchers and hindered amine light stabilizer (HALS) [25].

This study will investigate the effect of UV stabilizers on properties of PVC wood composites after natural weathering test. The main objective of this research is to study the effect of UV stabilizer types and loading on mechanical and physical properties of PVC/teak wood flour composites and PVC/corncob composites before and after natural weathering test.

#### **1.2 Objectives of the Research**

1. To study the effect of natural weathering test on the appearance and mechanical properties of PVC/wood flour and PVC/corncob composites.

2. To study the effect of UV stabilizer types and loading on the appearance and mechanical properties of PVC/wood flour and PVC/corncob composites before and after weathering test.

#### **1.3 Scopes of the Research**

- 1. The parameters that will be studied are
  - 1.1 Types of filler

- Teak wood flour, particle sizes of 250-425 µm and content of 60 phr.
- Corncob, particle sizes 250-425  $\mu m$  and content of 60 phr.
- 1.2 Types and loading of UV stabilizer;
- TiO<sub>2</sub> (R-101 and DLS 210), contents of 5, 10 and 15 phr.
- (Adding TiO<sub>2</sub> with only PVC/wood flour and testing for specific color change)
- 2-(2H-benzotriazol-2-yl)-p-cresol (Tinuvin P), contents of 1.0, 1.5 and 2.0 phr
- 2-(2H-benzotriazol-2-yl)-4, 6-ditertpentylphenol (Tinuvin XT 833), contents of 1.0, 1.5 and 2.0 phr.
- 2. Characterizations of PVC/wood flour and PVC/corncob composites, testing before and after natural weathering for 4 months;
  - 2.1 Mechanical properties are tested every month
  - Tensile properties
  - Flexural properties
  - 2.2 Color change are tested every week
  - 2.3 Surface chemical change
  - 2.4 Surface degradation

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### **CHAPTER II**

### THEORY

#### 2.1 Polyvinyl Chloride (PVC)

Polyvinyl chloride (PVC) is a major thermoplastic material finding uses in a very wide range of applications and products. The essential raw materials for PVC derived from salt and oil. The electrolysis of salt-water produces chlorine, which is combined with ethylene ( $C_2H_4$ ), obtained from oil, to form vinyl chloride monomer (VCM) [25]. The molecular structure of PVC is shown in Figure 2.1.



Figure 2.1 Molecular Structure of PVC

Moreover, molecules of VCM are polymerized to form PVC resin, in which appropriated additives are incorporated to make a customized PVC compound. Some additives are shown in Table 2.1.

Additives	Properties achieved	
Anti-oxidants &	Slow down the rate at which the polymer is degraded	
Stabilizers	by oxygen, heat, visible light or UV radiation	
Compatibilizers	Enable PVC to be mixed with other plastics and	
	Fillers	
Flame retardants	Reduce flammability of plastic	
Pigments	Colour the plastic	
Plasticizers	Produce flexible and manageable plastic	
Impact modifiers	Absorb shock without damage	
Fillers	Reduce cost, inert materials that simply add	
	to the plastic	

Nowadays, around 50% of manufactured PVC is used in construction replacing other materials such as wood or glass. PVC is strong, lightweight, durable and versatile. These characteristics make it ideal for window profiles. It can be used for flooring, windows, doorframes, waste pipes and electrical applications. PVC can be clear or colored, rigid or flexible, depending on the added additives and final application that needs to achieve [29].

#### 2.2 Natural Fibers and Their Chemical Compositions [3, 27]

The increased demand for the use of natural fiber as reinforcement and filler in wood plastic composites (WPCs) requires an in-depth understanding of the fiber material down to the ultra-structural level. Natural fiber is a complex substance constituted of cellulose, hemicellulose, lignin, pectin, waxes and water-soluble substances, with cellulose, hemicellulose and lignin as the basic components with regard to the physical properties of the fibers. Each of these components contributes to fiber properties, which ultimately impact product characteristics.

**2.2.1 Cellulose** is the major chemical component of fiber wall. It is composed of linear chains of D-anhydroglucopyranose units joined together by 1,4-β-D-glucan. The pyranose rings are in the  ${}^{4}C_{1}$  conformation, which means that the -CH<sub>2</sub>OH and -OH groups, as well as the glycosidic bonds, are equatorial with respect to the mean planes of the rings. Cellulose is the presence of both crystalline and amorphous regions within its microfibrils. The presence of crystalline cellulose, with regions of less order, and the size of the elementary fibrils work together to produce interesting combination of contrary properties such as stiffness and rigidity on one hand and flexibility on the other hand. Crystalline cellulose has a very limited accessibility to water and chemicals. Chemical attack can therefore be expected to occur primarily on amorphous cellulose and crystalline surface. Generally, the fibers contain 60-80 wt% of cellulose. However, hardwoods contain more cellulose than softwoods. The structure of cellulose is shown in figure 2.2.



Figure 2.2 Structure of Cellulose [27]

2.2.2 Hemicellulose is not a form of cellulose at all and the name is an unfortunate one. They comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The constituents of hemicellulose differ from plant to plant. The function of hemicellulose is less clear, there are existing some possibility that they serve as a temporary matrix before lignification. The hemicellulose differs from cellulose in three important aspects. In the first place they contain several different sugar units whereas cellulose contains only  $1,4-\beta$ -D-glucopyranose units. Secondly they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to one hundred times higher than that of hemicellulose. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it shows least resistance to them. Generally, wood contain the hemicellulose about 5 to 20 wt%. Hemicelluloses are more reactive than cellulose which is mainly due to their amorphous nature. The combination of cellulose and hemicellulose is known as holocellulose. The structure of hemicellulose is shown in figure 2.3.



Figure 2.3 Structure of Hemicellulose [27]

**2.2.3 Lignin** is widely distributed throughout the cell wall but it is highly deposited in the middle lamella region and accounts for 2 to 14 wt% of fiber. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. Their chief monomer units are various ring-substituted phenyl-propanes linked together by C-O-C and C-C linkages. However, these links are still not fully understood. Structural details are differ from one source to another. The mechanical properties are lower than those of cellulose. Lignin is thermally stable but is responsible for the UV degradation. The structure of lignin is shown in figure 2.4.



Figure 2.4 Structure of Lignin [27]

**2.2.4 Pectin** is a collective name for heteropolysacharides, which consists essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralization with alkali or ammonium hydroxide.

**2.2.5 Waxes** make up the part of the fibres, which can be extracted with organic solvents. These waxy materials consist of different types of alcohols, which are insoluble in water as well as in several acids.

#### 2.3 Wood Composite Matrices

A role of a matrix in a reinforced composite is to transfer stresses between the fibers, provide barrier against an adverse environment and protect the surface of the fibers from mechanical abrasion. The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major contribution for structures under bending loads, whereas influence on the interlaminar shear as well as on in-plane shear properties of the composite material. The interlaminar shear strength is an important design consideration while the in-plane shear strength is important for structures under torsional loads. The matrix provides lateral support against the possibility of fiber buckling under compression loading,

thus influencing to some extent the compressive strength of the composite material. The interaction between fibers and matrix is also essential in designing damagetolerant structure. The processability and defects in a composite material depend strongly on the physical and thermal characteristics, such as viscosity and melting point of the matrix. Additional functions of a matrix are to keep the fibers in place in the structure, to help distribute of transfer load, to protect the filaments, both in the structure and before fabrication, to control the electrical and chemical properties, and to carry interlaminar shear. Other desirable properties of a matrix with reasonable strength, modulus, and elongation, depending on the purpose of the structure, are to minimize moisture absorption, to wet and bond to fiber, to penetrate completely and eliminate voids during the compacting processes. The matrix should give strength at elevated temperature (depending on the application), low shrinkage and dimensional stability.

#### 2.4 Weathering of Wood [21]

Weathering is a general term used to define the slow degradation of materials exposed to the weather. The degradation mechanism depends on the type of material but the cause is a combination of factors found in nature: moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials and biological agents. Our houses are usually made of wood, and the outermost barrier to the weather is often wood or a wood-based product (siding, windows, decks, roofs, etc.). If these wood products are to achieve a long service life, we must understand the weathering process. Weathering is surface degradation of wood that is primarily initiated by solar radiation, but other factors are also important. The wetting and drying of wood through precipitation, diurnal and seasonal changes in relative humidity (RH), abrasion by windblown particulates, temperature changes, atmospheric pollution and oxygen contribute to the degradation of wood surfaces. However, it is the primarily ultraviolet (UV) portion of the solar spectrum that initiates the process we refer to as weathering. It is a photo-oxidation or photochemical degradation of the surface. The weathering process affects only the surface of the wood. The degradation starts immediately after the wood is exposed to sunlight. First, the color changes, then the

surface fibers are loosen and eroded, but the process is rather slow. On the other hand, wood decay is a process that affects the whole thickness or bulk of the wood. It is caused by decay fungi that infect the wood. *Decay fungi* are plants that grow through the wood cells and release enzymes that break down the wood components that they then metabolize for food. The critical factor for deterring their growth is to limit the water available to them. Wood cannot decay unless there is free water available in the wood cells. Free water is not necessary for weathering to occur, however the presence of water can help accelerate the process by causing splitting of the wood.

#### **2.5 Photo-Degradation of Polymers**

Photo-degradation (chain scission and/or crosslinking) occurs by the activation of the polymer macromolecule provided by absorption of photon of light by the polymer. In the case of photoinitiated degradation light is absorbed by photoinitiators, which are photocleaved into free radicals, which further initiate degradation of the polymer macromolecules. Photoaging is usually initiated by solar UV radiation, air and pollutants, whereas water, organic solvents and temperature. The general aspects of photo-degradation such as absorption of light, photophysical processes and photochemical reactions, kinetics and formation of oxidized group [7].

The photo-oxidation of most polymers proceeds by a radical chain mechanism, which involves the various steps common to chain processes; namely, initiation, propagation, possibly branching and termination.

Initiation

 $R - R \rightarrow 2R^{\bullet}$ 

Propagation

 $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ 

 $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$ 

 $R - H \rightarrow R^{\bullet}$ 

Chain branching

 $ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$  $2ROOH \rightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$  $RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$  $HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$ 

Termination

 $ROO^{\bullet} + ROO^{\bullet} \rightarrow$  radical destruction

Once a free radical is formed on a polymer chain C–H and C–C bonds on the carbon adjacent to the radical site which are subjected to cleavage as they have much lower bond dissociation energies than those associated with the primary polymer molecule. The reduction in the energy required to break these particular bonds results from the gain in energy when a new double bond is formed either to carbon as in reaction (a) example below or to oxygen in the case of alkoxy radicals undergoing  $\beta$ -scission as in reaction (b).



Chain scission is thus an expected degradation reaction in polymers whenever alkyl or alkoxy radicals are formed. [5]

#### **2.6 UV Stabilizers for Plastic Materials** [8, 25]

UV stabilizers are used to prevent or terminate the oxidation of plastics by ultraviolet (UV) light. They therefore act to protect the moulded product during its life, and are particularly used for building products. They act by absorbing of energy, deactivating the by-products of oxidation, and decomposing of by-products (or a combination of these). The action is similar to heat stabilizers and antioxidants, and some types of UV stabilizers also offer these functions. To be strictly accurate, UV affects all types of plastics, but a few (such as acrylonitriles and methyl methacrylates) show better resistance than most plasics. The UV part of sunlight (and in some instances UV light from artificial sources) breaks down the chemical bonds in a polymer in a process called photodegradation, ultimately causing cracking, chalking, colour changes, and loss of physical properties such as impact strength, tensile strength, elongation, and others. UV radiation can cause colour change and degrade which are used physical properties, especially in polyolefins, ABS, PVC, PC, and PU. Stabilizers to protect plastics compounds against the effect of UV light (especially sunlight) prevent oxidation from that source. The most important types of light stabilizers are ultraviolet light absorbers, energy transfer agents or quenchers, as well as hindered amine light stabilizers (HALS). A brief description of these different light stabilizers is as follows.

#### 2.6.1 UV Light Absorbers

UV stabilizers are used to prevent or terminate the oxidation of plastics by UV light. They therefore acts as protector to moulded product during its life, and are particularly used for building products. They act by absorbing of energy, deactivating the by-products of oxidation, and decomposing of by-products (or a combination of these).

UV light absorbers convert harmful ultraviolet radiation to harmless infrared radiation or thermal energy, which is dissipated through the polymer matrix. They can be either transparent as hydroxybenzophenone, benzohydroxyphenylbenzotriazole or opaque as carbon black and titanium dioxide (TiO<sub>2</sub>).

#### i) Titanium dioxide (TiO<sub>2</sub>)

Rutile titanium dioxide absorbed ultraviolet in the 300 to 400 nm range. It helps polymer to prevent the photo-degradation.

#### ii) Hydroxybenzophenone and hydroxyphenylbenzotriazole

These well-known UV absorber types offer the advantage of being suitable for natural or transparent applications. To provide good protection to the plastic material, a certain absorption depth is needed which makes these absorbers inefficient in thin items such as films (below 100 micron).

#### iii) Carbon black

Carbon black is one of the most efficient and widespread light absorber. Typical applications for carbon black as a UV stabilizer in plastics are exterior pipe, polyolefin agricultral film, automotive and exterior cable jacketing.

#### 2.6.2 Quenchers

This type of light stabilizer functions by bringing 'excited' state polymer molecules (chromophores) back to their stable state, preventing bond cleavage and finally formation of free radicals. Nickel stabilizers are typical used as quenchers.

#### 2.6.3 Hindered Amine Light Stabilizers (HALS)

These efficient light stabilizers do not change the color of plastic material and are suitable for both thin and thick material. HALS is not active by absorbing the UV radiation but rather by reacting with the radicals, which are formed, and thus by limiting the degradation reactions in the presence of some chemicals.

The effectiveness of HALS systems does not depend on the thickness of the plastics product and they are therefore particularly useful for protection of surface layers and in thin sections. Agents are of low or high molecular weight. Polymeric HALS offer superior compatibility, low volatility, excellent resistance to extraction, and contribute to heat stability.

#### 2.7 Weathering Test Methods [25]

Besides natural weathering, several test methods have developed using artificial light sources to provide accelerated test procedures. All methods are based on the regular observation of characteristics reflecting an aging process such as the mechanical properties (elongation at break, tensile properties or impact strength) or visible characteristics, such as crack formation, chalking, changes in color or gloss.

The main testing methods for aging of plastic material are as follows

- 2.6.1) Natural weathering
- 2.6.2) Artificial accelerated weathering chambers:
- Fluorescent ultraviolet
- Xenon arc

#### 2.7.1 Natural Weathering

Outdoor exposure is performed on samples mounted on testing racks oriented under standard conditions (horizontal, 45° or 90° tilt). For example 45° tilt is shown in Figure 2.5. In this way, the material is exposed to the full radiation spectrum from the infrared to the ultraviolet ranges. Of course, not only radiation but also temperature and relative humidity levels strongly depend on the location, the seasons, which can show some fluctuation from year to year.



Figure 2.5 Natural Weathering Test [25]

#### 2.7.2 Artificial Weathering Chambers

#### i) Fluorescent ultraviolet chamber

The device simulates the effect of sunlight with fluorescent ultraviolet (UV) lamps, while rain and dew are simulated by the condensation of humidity. The UV light only represents roughly 5% of the sunlight but it is responsible for most of the polymer degradation. In addition, materials are often tested with equipment, which simulate only the shortest wavelengths (UV). The UV-B range includes the shortest wavelengths found in sunlight. Therefore, for many applications, it is a fast and efficient method. The fluorescent ultraviolet chambers are shown in Figure 2.6.



Figure 2.6 Fluorescent Ultraviolet Chambers [25]

#### ii) Xenon arc weathering chamber

Among all artificial UV sources, Xenon lights provide the best simulation of natural sunlight. The Xenon arc weathering chambers have automatic control of light intensity, temperature and humidity. Specific programs allow the samples to be sprayed with water or exposed to alternating cycles of dark and light periods. The xenon arc weathering chamber is shown in Figure 2.7.



Figure 2.7 Xenon Arc Weathering Chambers [25]

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#### **CHAPTER III**

#### LITERATURE REVIEW

Nowadays, the research in wood plastic composites (WPCs) is growing rapidly. The several applications of WPCs are used in exposure to the outdoor environments with caused degradation of products. Therefore, it is essential to study the factors of degradation and improve the durability of WPCs.

There were several researches studied the degradation of WPCs. The weathering test is one way to examine the degradation of plastic materials. The main testing methods for plastic materials are natural weathering [10, 22] and artificial accelerated weathering chambers such as fluorescent light source [1, 11, 12] and xenon arc [10, 16, 17, 18, 20]. Sinmazcelik (2004) [22] showed that the resistance to natural weathering of polyphenylene sulfide (PPS) after reinforced with calcium carbonate (CaCO<sub>3</sub>). CaCO<sub>3</sub> in the composite reduced the degradation process which was shown in the value of impact strength.

The factors of degradation of WPCs before and after weathering are ultraviolet (UV), rain and content of fillers. Nicole and Laurent (2006) [18] reported that the high density polyethylene/wood flour composites (HDPE/WF), which were exposed to UV radiation with water spray, showed greater discoloration and more flexural and strength loss than those exposed to UV radiation alone. The content of fillers was an important factor on the properties after weathering of WPCs. When the fillers content (wood or natural fiber) and the exposure time were increased the concentrations of oxidative products (carbonyl index) were also increased [12, 10], as shown in figure 3.1 [12]. Therefore, the specimens with higher wood flour content showed more color fade than the specimens with lower wood flour content [10, 12, 20], as shown in figure 3.2 and 3.3. Figure 3.2 showed the brightness of polypropylene (PP) with different content of wood after weathering test for 1500 hrs of accelerated weathering. The brightness of PP containing 20 wt% wood showed smallest value but

PP containing wood at content of 30, 40 and 55 wt% showed a little difference in brightness [9]. Moreover, Figure 3.3 showed color fade in both of HDPE and PP containing wood flour at content of 50 and 70 wt%. The color fade of both of HDPE and PP content 70 wt% wood showed higher than brightness that containing 50 wt% wood [20].



Figure 3.1 Normalized carbonyl absorption at 1730 cm<sup>-1</sup> (carbonyl index) as a function of wood flour contents and weathering times. The accelerated weathering tests were completed after 400 hours ( $t_{400}$ ) and 2600 hours ( $t_{2600}$ ) of UV/condensation cyclic exposures [12]



Figure 3.2 Brightness of WPCs with different ratios of wood and polypropylene (PP) during 1500 h of accelerated weathering [10]



Figure 3.3 Effect of content of wood flour on color fade of wood flour-plastic composites [20]

In addition, the method to improve the durability is to add additives in plastic materials such as UV stabilizers [1, 10, 11, 15, 16, 18] and colorants [10, 16, 20]. Nicole and Laurent (2003) [20] reported that the HDPE/wood flour composites with colorant and 2-(2H-benzotriazole-2-yl)-4,6-ditertpentylphenol (ultraviolet absorber, UVA) showed smaller color change than that with hindered amine light stabilizer (HALS) after weathering test. Nicole and Laurent (2006) [18] also reported the HDPE/WF composites adding a hydroxyl phenyl benzotriazole (UVA) and zinc ferrite pigment (P) resulted in less lightening of composites after 3000 hrs of exposure to UV radiation and water spray. Increasing the content of UVA the amount of lightening does not change, while increasing the content of P resulted in less lightening. Moreover, the composites which combinations of UVA and P resulted the smallest lightening. Muasher and Sain (2005) [15] reported that the HDPE/WF composites which combination of a benzotriazole, UV absorber (UVA) and diester HALS shows synergistic effect on decreasing color fading.

In addition, the composite with dark pigment exhibited smaller color change than that with light pigment and unpigment, [10, 20] as shown in figure 3.4.



Figure 3.4 Color change of pigmented wood-fiber composites (WPCs) exposed to natural weathering for 24 months [10]

WPCs also improve the durability of the mechanical properties by adding UV stabilizer. The flexural modulus and flexural strength of HDPE/WF composites decreases as the following additives were used; i.e. colorlant, UV absorber (UVA), high molecular weight hindered amine light stabilizer (LS1) and low molecular weight hindered amine light stabilizer (LS2) respectively [16]. Moreover, the best resulted were adding combinations of UVA and P showed highest retain flexural strength and flexural modulus of WPCs.

Polyvinyl chloride is sensitive to UV radiation. Laurent et al (2000) [11] found that the PVC/wood fiber composites with titanium dioxide (TiO<sub>2</sub>) were smaller discoloration than PVC/ wood fiber composites without  $TiO_2$ .

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### **CHAPTER IV**

### **EXPERIMENTS**

#### **4.1 Materials**

#### 4.1.1 PVC Resin

PVC resin and additives are supplied by Vinythai Company Limited.

PVC;

- Suspension PVC resin (Siamvic 258 RB)

Additives;

- Heat stabilizer
- Processing aid
- Internal lubricant
- External lubricant

4.1.2 Fillers (particle size 250-425 µm and content of 60 phr)

- Teak wood flour
- Corncob

#### 4.1.3 UV Stabilizers

4.1.3.1 Titanium dioxide (TiO<sub>2</sub>)

Both R-101 and DLS 210 grades are obtained from Dupont (Thailand) Company Limited [31].

i) TiO<sub>2</sub> (R-101)

TiO<sub>2</sub> (R-101) is a rutile titanium dioxide pigment manufactured

by the chloride process. It is excellent for high- temperature plastic applications

requiring outstanding dispersibility and lowest possible volatility. The grade is affined, dry white powder with the properties shown in Table 4.1. A rutile structure of  $TiO_2$  is shown in Figure 4.1.

Table 4.1 Properties of R-101 UV Stabilizer [31]

Properties	Value
Titanium Dioxide, wt%, min.	97
Alumina, wt%, max.	1.7
Organic Treatment, wt%, carbon	0.2
Specific Gravity, g/cc	4.2
Mean Particle Size, nm	290



Figure 4.1 Crystal Structures of Rutile Type of Titanium Dioxide [33]
### ii) TiO<sub>2</sub> (DLS 210)

DLS 210 has been shown to be a stronger UV screener on an equal weight basis than typical organic UV absorbers like benzophenones and benzotriazoles. It has broad-spectrum UV screening capability, able to attenuate UV across both the UVA and UVB regions. The properties of DLS 210 is shown in Table 4.2

Table 4.2 Properties of DLS 210 UV Stabilizer [31]

Properties	Value
Titanium dioxide, wt%, min.	85
Alumina, wt%, max.	10
Spacific gravity g/cc	3.7
Mean particle size, nm	135
Bulk density, g/cc	0.45

4.1.3.2 2-(2H-benzotriazol-2-yl)-p-cresol (Tinuvin P) is supplied by Ciba Specialty Chemicals (Thailand) Limited [26].



Figure 4.2 Molecular Structure of Tinuvin P UV Stabilizer

Tinuvin P feathers a strong absorbtion of ultraviolet radiation in the 300-400 nm. It also has a high degree of photo-stability over long periods of light exposure. Reducing and oxidizing agents used in polymerization and curing processes have no effect on the stability of Tinuvin P. Properties of Tinuvin P is shown in Table 4.3.

Properties	Value
Colour	Slightly yellow
Molecular weight	225 g/mol
Melting range	128-132 °C
Flashpoint	205 °C
Specific gravity (20 °C)	$1.38 \text{ g/cm}^3$

Table 4.3 Properties of Tinuvin P UV Stabilizer [26]

4.1.3.3 2-(2H-benzotriazol-2-yl)-4, 6-ditertpentylphenol (Tinuvin XT 833) is supplied by Ciba Specialty Chemicals (Thailand) Limited [26].

Molecular Formula: C<sub>22</sub>H<sub>29</sub>N<sub>3</sub>O



Figure 4.3 Molecular Structure Tinvin XT 833 UV Stabilizer

Tinuvin XT 833 is a powerful ultraviolet light stabilizer that maintains its activity in hightly acidic environment. It protects PVC from the harmful effects of light exposure and helps it maintain its initial appearance, its initial tensile, elongation, and impact properties and its physical integrity during long-term weathering. The properties of Tinuvin XT 833 are shown in Table 4.4.

Properties	Value		
Colour	White to off-white		
Molecular weight	351.49 g/mol		
Melting range	63-75 °C		
Bulk density	488 g/L		

Table 4.4 Properties of Tinuvin XT 833 [26]

### 4.2 Preparation of PVC Dry Blend

The dry blending process and the concentrations of PVC, heat stabilizer, processing aid, external lubricant and internal lubricant were kept constant as the formulation shown in Table 4.5.

Table 4.5 PVC Dry Blend Formulation

Ingredients	Concentration (phr)
PVC	100
Heat stabilizer	4
Processing aid	6
External Lubricant	9101225
Internal Lubricant	0.5

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### 4.3 Preparation of PVC/Wood and PVC Natural Fiber Composites

Before mixing, teak wood flour and corncob with particle sizes 250-425  $\mu$ m (40-60 mesh) and a fixed content of 60 phr are dried in a oven at 105 °C for 12 hours. Then PVC dry blend is mixed with fillers and UV stabilizer in a two- roll mill (Labtech) and the roll gap was 0.3 mm. The temperature in both of front roll and back roll were 170 °C for 5-6 min. After mixing, the sample was compression molded into steel mold. The size of specimen was 200\*200\*4 mm<sup>3</sup>. The temperature in both of upper heater and lower heater were 170 °C under pressure 150 psi for 4 min. The specimens were cut into test pieces for mechanical and physical property test.

### 4.4 Characterization

### 4.4.1 Natural Weathering

Natural weathering test is used to evaluate the stability of plastic materials when exposed to outdoor environment. The relative durability of plastics in outdoor use can be very different depending on the location of the exposure because of differences in ultraviolet (UV) radiation, time of wetness, temperature and pollutants. Following ASTM 1435, specimen holders should be used to support the many sizes of specimens involved in this testing. The direction of exposed can be horizontal and experiment was performed in Thailand, during December 2007 to March 2008. The color change and mechanical properties of samples were determined weekly and monthly, respectively. The sample for mechanical and color change testing exposed at Bangkok and Rayong, respectively. The meteorological and radiation data were shown in Table 4.6 and 4.7, respectively.

Month	Mean Temperature (°C)	Total Rain (mm)	Rainy Day	Mean Humidity (%)	Mean Sunshine/day (hrs)
December (2007)	28.9	0	0	61.0	8.3
January (2008)	27.8	62.1	1	63.0	8.2
February (2008)	27.8	69.3	9	70.0	6.4
March (2008)	29.5	3.6	3	67.1	8.3

Table 4.6 The Meteorological and Radiation Data in Bangkok [34]

 Table 4.7 The Meteorological and Radiation Data in Rayong [34]

Month	Mean Temperature (°C)	Total Rain (mm)	Rainy Day	Mean Humidity (%)	Mean Sunshine/day (hrs)
December (2007)	27.0	0	0	70.0	8.8
January (2008)	<mark>26</mark> .8	0	0	69.0	8.5
February (2008)	26.8	75.1	11	75.0	6.5
March (2008)	28.2	37.6	3	73.8	8.2

### 4.4.2 Scanning Electron Microscope (SEM)

Scanning Electron Microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM equipment shown in Figure 4.4. uses electrons for imaging, same as a light microscope uses visible light. The advantages of SEM over light microscopy include greater magnification and much greater depth of field. Test specimens are sputter coated with gold, then placed in a vacuum chamber for viewing on the computer monitor at up to 10,000x magnification [32].



Figure 4.4 Scanning Electron Microscopy (SEM) [32]

### 4.4.3 Fourier Transform Infrared Spectrometry (FTIR)

FTIR spectroscopy was conducted on a Nicolet 6700 spectrometer to determine the functional groups at surface of the samples before and after weathering. The spectrum was averaged from 100 scans recorded in absorbance units from 4000 to 700 cm<sup>-1</sup> using attenuated total reflectance (ATR) mode. The surface of sample was contacted with diamond crystal. The occurrences of surface oxidation of sample was monitored by a carbonyl group change. The sharp bands at 1715 cm<sup>-1</sup> and 2912 cm<sup>-1</sup> were due to C=O stretching and C-H stretching, respectively.



Figure 4.5 Transform Infrared Spectrometry (FTIR) [32]

### **4.4.4 Tensile Properties**

This test method covers the determination of the tensile properties of both unreinforced and reinforced plastics. The tensile test provides tensile strength (at yield and at break), tensile modulus, stress-strain, elongation at yield and elongation at break. The dog-bone shape specimens are prepared following ASTM 638. The specimens are measured by a universal testing machine (Instron 5567, NY, USA) as shown in Figure 4.6.



Figure 4.6 Universal Testing Machine (Instron 5567, NY, USA)

### **4.4.5 Flexural Properties**

The Flexural test measures the force required to bend a beam under 3 point loading conditions. The data is often using to select materials for parts that will support loads without flexing. Flexural modulus is used as an indication of a material's stiffness when flexed. The parameters for this test including a support span of 48 mm, speed of loading 1.2 mm/min with a load cell of 1 kN. The specimen size is 10x4x80 mm<sup>3</sup>, following ASTM D 790 using a universal testing machine (Instron 5567, NY, USA) as shown in Figure 4.7.



Figure 4.7 Flexural Testing

### 4.4.6 Color Measurements

This test method was originally resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference  $\Delta E_{ab}^*$  between two colors each given in terms of lightness (L\*) and chromaticity coordinate ( a\* and b\*) is calculated following ASTM D 2244 by Ultrascan pro in CIE color system.

$$dE^* = [(dL^*)^2 + (da^*)^2 + (db^*)^2]^{1/2}$$

The magnitude of  $dE_{ab}^*$ , gives no indication of the character of the difference since it does not indicate the relative quantity and direction of hue, saturation, and lightness differences. The direction of the color difference is described by the magnitude and algebraic signs of the component dL\*, da\* and db\*.

$$dL^* = L_1^* - L_0^*$$
$$da^* = a_1^* - a_0^*$$
$$db^* = b_1^* - b_0^*$$

Where  $L_0^*$ ,  $a_0^*$  and  $b_0^*$  refer to the initial, and  $L_1^*$ ,  $a_1^*$  and  $b_1^*$  refer to the final specimen. The signs of the components dL\*, da\* and db\* have the following approximate meanings;

+da\* = redder (less green)
-da\* = greener (less red)
+db\* = yellow (less blue)
-db\* = bluer (less yellow)



### **CHAPTER V**

### **RESULTS AND DISCUSSION**

Polymer used in this study was suspension polyvinyl chloride (PVC) resin (Siamvic 258 RB). Teak wood flour (TWF) and corncob (CC) with particle sizes 250-425  $\mu$ m (40-60 mesh) and a fixed content of 60 phr were used as fillers. PVC/TWF and PVC/CC composites with and without UV stabilizer were prepared by two-roll mill at 170 °C for 5-6 minutes and compression molded under pressure 150 psi for 4 minutes. In this study, the effect of types and loading of UV stabilizer on PVC/TWF composites and PVC/CC composites were examined by the changes in their appearance and mechanical properties before and after natural weathering test for 4 months. The color change was determined every week by ultrascan pro (USP, 1259), whereas tensile and flexural properties of samples were tested every month by Universal testing machine (Instron, 5567). A scanning electron microscope (SEM) (Joel, JSM 5800, LV) was used to investigate surface degradation. Furthermore, surface chemical change was determined by mean of Fourier Transform Infrared Spectrometry (FTIR) (Nicolet 6700).

Full Name	Abbreviation	Loading (phr)
R-101 (TiO <sub>2</sub> )	Til	5, 10, 15
DLS 210 (TiO <sub>2</sub> )	Ti2	5, 10, 15
Tinuvin P	P	1.0, 1.5, 2.0
Tinuvin XT 833	XT	1.0, 1.5, 2.0

It can be noted that the abbreviation in this chapter refers to full name of UV stabilizers as follow:

For example, PVC/TWF+XT/1.0 is PVC dry blend filled with teak wood flour and 1.0 phr Tinuvin of XT 833 stabilizer.

### 5.1 Fourier Transform Infrared Spectroscopy (FTIR)

Surface of PVC and PVC composites were examined using FTIR spectroscopy. The absorption band which interests us was at 1800-1680 cm<sup>-1</sup> associated with carbonyl (C=O) groups. The increase of carbonyl groups for PVC and PVC composites assigned that surface oxidation increased [6].





**Figure 5.1:** FTIR spectra of a) PVC and b) PVC/TWF composites without UV stabilizer unweathered and weathered for 4 months. A and B represents the spectrum of sample weathered (bottom surface) to UV radiation for 4 months and unweathered whereas C and D are spectrum of samples weathered (top surface) to UV radiation for 2 and 4 months.

Figure 5.1a) and 5.1b) show the FTIR spectra of PVC without UV stabilizer and PVC/TWF composites without UV stabilizer unweathered and various weathered periods. The spectrum of unweathered PVC without UV stabilizer showed that the absorption band at 1728 cm<sup>-1</sup> (C=O stretching) slightly increased. PVC without UV stabilizer weathered to environment for 4 months showed the highest absorption band 1728 cm<sup>-1</sup>. However, exposure time to UV radiation significantly increased the absorption band 1728 cm<sup>-1</sup> increased. Similar behavior was also found by Nicole et al (2004). The increase in the concentration of carbonyl group of polymer after

weathering is the indication of the number of chain scissions that occur in polymer as discussed in the work of Nicole et al [17]. For both PVC and PVC/TWF composites exposed to UV radiation at various time it can be seen that the slightly drop of the height of the absorption band assigned to C-H stretching (2912 cm<sup>-1</sup>) occurred due to the polymer chain scission [9]. The FTIR spectra suggest that the mechanism of the photo-degradation of PVC/TWF composites without UV stabilizer showed the similar trend as that of PVC without UV stabilizer. As the exposure time to UV radiation increased the intensity of absorption band at 1728 cm<sup>-1</sup> also increased for PVC/TWF composites. The increase in this band of PVC/ TWF composites at various weathered times showed the higher intensity than that of PVC without UV stabilizer. The absorption band at 1728 cm<sup>-1</sup> may be assigned the concentration of carbonyl group on the surface and indication of oxidative photo-degradation. Moreover, it can be used as supporting evidence of the chemical composition changes on the surface of weathered samples. The photo-oxidation degradation was also noticed, to a certain extent, by the formation of unsaturated vinyl groups (1616-1650 cm<sup>-1</sup>) in FTIR spectra of exposed samples [12]. Carbonyl group and vinyl group formation implied polymer chain scission [17]. The chain scission occurs, as evidenced by an increase in concentration of carbonyl and vinyl group and a decrease in molecular weight. These authors concluded that shorter chains have higher mobility and crystallized readily. As UV radiation exposure continues, chain scission continues to effect molecular weight and crystallinity, which lead to the embrittlement [16]. In addition, for PVC/TWF composites without UV stabilizer, the concentration of carbonyl group of the composite weathered (bottom surface) to UV radiation for 4 months showed the higher intensity than that of unweathered the composite but smaller intensity than that of the composites without UV stabilizer weathered (top surface) to UV radiation for 4 months. The data indicate that UV radiation can penetrate through the matrix of PVC/TWF composites.



**Figure 5.2:** FTIR spectra of PVC and PVC composites without UV stabilizer weathered for 4 months

Figure 5.2 shows the effect of filler types on the concentration of carbonyl group of PVC after weathering for 4 months. The absorption band at 1728 cm<sup>-1</sup> of both of PVC/TWF composites and PVC/CC composites was higher than that of PVC without UV stabilizer because wood flour and corncob contains oxidized compounds such as carbonyl groups. It is noticed from Figure 5.2 that the concentration of carbonyl groups has increased after incorporating CC and TWF into the PVC matrix. Therefore, the present of TWF and CC substantially accelerates the photo-degradation of the PVC matrix [11]. Moreover, the oxygen is the factor of the degradation on WPCs. Therefore, the addition of wood flour into polymer matrix increased the amount of oxygen in the sample, including carbonyl group. The absorption bands at



 $\rm cm^{-1}$  (carbonyl group) of both PVC/CC and PVC/TWF composites showed a slight difference.





The degradation factors of wood plastic composites (WPCs) are UV radiations, atmospheric oxygen, moisture and pollutants. The UV radiation is the important factor to degradation process. The addition of UV stabilizers is the alternative method to develop the durability of WPCs because UV stabilizer can protect WPCs from harmful effects of UV radiation. Figure 5.3 shows the effect of UV stabilizer types and loading on the concentration of the carbonyl group of PVC and PVC/TWF composites after weathering test for 4 months. Figure 5.3a) shows the concentration of carbonyl group of PVC with and without UV stabilizer. The intensity of the absorption band at 1728 cm<sup>-1</sup> of PVC with XT stabilizer at the loading of 1.0, 1.5 and 2.0 showed a little difference and was smaller than that of PVC without UV stabilizers. Figure 5.3b) shows the concentration of carbonyl group of PVC/TWF

composites with and without UV stabilizers. The intensity absorption band of PVC composite showed the similar trend as that of PVC. The intensity absorption band at 1728 cm<sup>-1</sup> of PVC/TWF composites with a XT stabilizer at loading of 1.0, 1.5 and 2.0 phr showed a little difference and was smaller than that of PVC/TWF composites without UV stabilizer. Both Figure 5.3a) and 5.3b) indicated that UV stabilizer can prevent or delay the formation of carbonyl group of PVC and PVC/TWF composites. Moreover, PVC/TWF composites with UV stabilizer showed higher concentration of carbonyl group than that of PVC with UV stabilizer. The reason to explain this phenomenon is similar to that for Figure 5.2. Moreover, all of loading showed little difference intensity of carbonyl group. The effect of UV stabilizer type at 1 phr loading is shown in Figure 5.3a). It can be seen that the concentration carbonyl group of PVC with P and XT stabilizer showed slight difference. In Figure 5.3b), the concentration of carbonyl group of PVC/TWF composites with P and XT stabilizers at loading of 1 phr are similar which is consistent with the result in Figure 5.3a. Nicole and Laurent (2003) [16] reported that UV absorber can delay the degradation of WPCs more than HALS because HALS protection as free-radical scavenger but that does not absorb UV radiation. Moreover, Muasher and Sain (2006) [15] studied the effect of photo-stabilizer on the color change of wood filled plastic composites. The UVA and UVB regions are defined as the radiation in the rang of 320-400 and 290-320 nm, respectively. UVB radiation is absorbed by ozone layer in the stratosphere but most of the UVA radiation reaches the earth's atmosphere, it is expected that the UV stabilizers which can absorb radiation in UVA region will have a greater effect on photo-oxidation than UVB radiation [15]. In this study, both P and XT stabilizers are benzotriazole stabilizer and absorb radiation in the UVA region [26]. Therefore, they showed the similar effect on the concentration of carbonyl group of composites.

### **5.2 Color Analysis**

UV radiation can cause the change in the surface chemistry of PVC and PVC composites, which may lead to change in color of the samples. It was also known as photo-degradation. In this study, PVC and PVC composites were exposed to outdoor environment by natural weathering test. The effects of UV stabilizer types and loadings on the color change of PVC and PVC composites were studied. The ultrascan pro (USP 1259) was used to determine color change according to the CIE  $L^*$  a\* b\* color system.





**Figure 5.4:** a) Lightness change and b) Color change of PVC with and without UV stabilizers after exposed to sunlight

The color change (dE\*) of the samples was determined based on three color parameters: L\*, a\* and b\*. The lightness change (dL\*) were the most important parameters influencing of dE\*, the trend of dL\* would be related to dE\*. An increase in the L\* values (+dL\*) refers the samples lightening or fading, and a decrease in the L\* values (-dL\*) refers the samples darkening. Figure 5.4a) shows the lightness change of PVC with and without UV stabilizers at various loadings. The lightness change decreased with increasing exposure time. It can be noticed that the lightness greatly decreased during the first week. During the  $2^{nd}$  week and the  $16^{th}$  week, PVC with UV stabilizer showed small lightness change. On the other hand, PVC without UV stabilizer greatly decreased during exposure to sunlight up to 16 weeks. Moreover, at the  $16^{th}$  week, the lightness changes of PVC without UV stabilizer and PVC with 2 phr of XT stabilizer were -17.2 and -2.2 respectively. The lightness change of PVC without UV stabilizer showed 8 times higher than that of PVC with 2 phr of XT stabilizer. The lightness change of all loading was slightly different. The color change showed the similar trend as that of lightness change. From Figure 5.2b) the color change of PVC without UV stabilizer greatly increased. The PVC with UV stabilizer both P and XT stabilizers shows a little difference of color change after exposed to sunlight. At 16 weeks the color changes of PVC without UV stabilizer and PVC with 2 phr of XT stabilizer were 17.3 and 2.6 respectively. The color change of PVC without UV stabilizer was 7 times higher than that of PVC with 2 phr XT of stabilizer. When the polymer is exposed to UV radiation the color change occurs rapidly due to the formation of alkene linkages and the resulting dehydrogenation of the allylic chrorides in the polymeric matrix [11]. The results indicated that the UV stabilizer can help delay change in color of polymer. P and XT stabilizers absorbed radiation in UVA region. Therefore, both P and XT stabilizers can improve the photostability of PVC. In addition, the number of alkyl group in UV stabilizer had no significant effect on the color change of PVC.





**Figure 5.5:** a) Lightness change and b) Color change of PVC/TWF composites with and without  $TiO_2$  after exposed to sunlight

Figure 5.5a) shows the lightness change of PVC/TWF composites with and without Ti1 and Ti2 stabilizers. PVC/TWF composites without TiO<sub>2</sub> pigment showed the highest lightness change. PVC/TWF composites with higher TiO<sub>2</sub> pigment showed the smaller lightness change. Moreover, the lightness change at various exposure time of the PVC/TWF composites with Ti1 (particle size 290 nm) and Ti2 (particle size 135 nm) stabilizers at 15 phr showed similar trend. The trends of the color change in Figure 5.5b) are similar to that in Figure 5.5a). The color change of PVC/TWF composites without TiO<sub>2</sub> and PVC/TWF composites with Ti2 stabilizer at loading of 15 phr were 32.3 and 8.2 respectively. The color change of PVC/TWF composites with 15 phr of Ti2 stabilizer. The color change was decreased with increasing TiO<sub>2</sub>. The TiO<sub>2</sub>

loading had higher effect on the color change than the particle size of  $TiO_2$ . The PVC/TWF composites with  $TiO_2$  showed muddy color unlike the natural wood color. Rutile  $TiO_2$  absorbs UV radiation in the range of 300 to 400 nm [25]. The light stability of composites can be improved with rutile  $TiO_2$  stabilizers as discussed in the work of Laurent et al [11]. Moreover, the presence of  $TiO_2$  helped blocking the penetration of UV radiation and masked the bleaching of WPCs.



**Figure 5.6:** The lightness change of PVC/TWF composites with and without UV stabilizers after exposed to sunlight

Figure 5.6 shows the lightness change of PVC/TWF composites with and without UV stabilizers after exposed to sunlight. It can be observed that the lightness change greatly increased during exposed to sunlight up to 4 weeks. After 4 weeks the lightness change of PVC without UV stabilizer was slightly changed. After exposed to sunlight for 16 weeks, PVC/TWF composites with and without UV stabilizer showed the a little difference of lightness change. At the exposure period of 16 weeks, PVC/TWF composites with XT stabilizer at various loadings showed a little difference of the lightness change. Moreover, PVC/TWF composites with P and XT stabilizer at 1 phr showed a little difference of lightness change. UV stabilizer can decrease the oxidative degradation of plastic and plastic-based composites. However, they do not always significantly change the fading of WPC material [2].



**Figure 5.7:** The lightness change of PVC/TWF composites and PVC/CC composites with and without UV stabilizers after exposure to sunlight

Figure 5.7 shows the lightness change of PVC/CC composites and PVC/TWF composites with and without UV stabilizer after exposed to sunlight. PVC/CC composites at 1 phr of XT stabilizer and without UV stabilizer at 16<sup>th</sup> week showed a little difference of lightness change. Moreover, the lightness of PVC/TWF composites with and without UV stabilizers showed the similar trend as that of the lightness change of PVC/CC composites. In comparison between PVC/CC composites and PVC/TWF composites without UV stabilizers, the lightness change of PVC/TWF composites and PVC/CC composites were 35.6 and 10.5 respectively. The lightness change of PVC/TWF composites showed 3 times higher than that of PVC/CC composites. During exposure to sunlight, lignin and hemicelluloses in wood fiber were degraded by UV radiation. Subsequently, the main chemical component at

WPC surface is possibly cellulose, which is fade and comparatively stable against UV [10]. The lignin of the teak wood and corncob were 34 %wt [30] and 23 %wt [13] respectively as shown in Table 5.1. Hence, the higher the amount of the lignin in wood, the more gap of fading after exposing to sunlight would occur.

Fiber Compositions (%)	Corncob [13]	Teak Wood [30]
Cellulose	34	41.7
Hemicellulose	40	-
Lignin	23	34
Ash	1.5	1.8
Other	1.5	22.5





**Figure 5.8:** Surface texture of PVC with and without UV stabilizer a) PVC without UV stabilizer before weathering b) PVC without UV stabilizer after weathering for 4 months c) PVC+XT/1 before weathering d) PVC+XT/1 after weathering for 4 months



**Figure 5.9:** Surface texture of PVC/TWF composites with and without UV Stabilizer a) PVC/TWF composites before weathering b) PVC/TWF composites after weathering for 4 months c) PVC/TWF+XT/1 before weathering d) PVC/TWF+XT/1 after weathering for 4 months



**Figure 5.10:** Surface texture of PVC/CC composites with and without UV stabilizer a) PVC/CC composites before weathering b) PVC/CC composites after weathering for 4 months c) PVC/CC+XT/1 before weathering d) PVC/CC+XT/1 after weathering for 4 months

The effect of UV stabilizers on color change was supported by Figure 5.8-5.10. Figure 5.8 shows the color change of PVC. The PVC without UV stabilizer renders highest color change after weathering for 4 months as shown in Figure 5.8b). On the other hand, from Figure 5.8c) and 5.8d) the PVC with UV stabilizer before and after weathering showed a little difference of color change. From Figure 5.9b) and 5.9d) PVC/TWF composites with and without UV stabilizers after weathering test showed a little difference in color change.

Finally, the results on color change of PVC/CC composites show the same trend as the results of PVC/TWF composites. After weathering test the PVC/CC composites with (Figure 5.10b)) and without (Figure 5.10d) UV stabilizer showed a little difference of color change. Hence, the UV stabilizer can only prevent the color change on polymer and had small effect on filler.

### **5.3 Flexural Property Analysis**

### **5.3.1 Flexural Strength**

The problem for the outdoor applications of WPCs is that terrestrial sunlight can cause photo-degradation. The photo-degradation of both the polymer matrix and wood fiber when exposed to sunlight had many factors such as long-term solar ultraviolet (UV) radiation, rain and pollutants [1]. Exposure to UV radiation can cause changes in both the polymer matrix and wood component. Photo-degradation of polymer results in free radical generation, which may conduct to terminate via crosslinking or chain scission. Moreover, the surface cracking and loss in strength and stiffness occurred [19].



**Figure 5.11:** Change in flexural strength of PVC with and without UV stabilizer after exposed to sunlight

Figure 5.11 shows the change in flexural strength of PVC with and without UV stabilizer after exposed to sunlight. The flexural strength of PVC without UV stabilizer decreased from 79.5 MPa to 69.0 MPa (approximately 13% decrease) after exposure to sunlight for 4 months. The flexural strength of PVC with 1 phr of XT stabilizer decreased from 79.4 MPa to 75.0 MPa (approximately 6% decrease) after exposed to sunlight. PVC with UV stabilizer had higher ability to maintain the flexural strength than the PVC without UV stabilizer after exposed to sunlight. There was no significant difference observed in the systems of PVC with and without UV stabilizers at various XT stabilizer loadings for 1 month exposure. However for 2 month exposure, the flexural strength of PVC at 1.5 and 2.0 phr of XT stabilizer had smaller decrease than that of PVC with 1.0 phr of XT stabilizer. Between 2 and 4

months exposed time, the flexural strength of PVC with any XT stabilizer contents showed little difference. In comparison between PVC with P and XT stabilizer at 1 phr after exposed to sunlight up to 4 months, their flexural strengths were not difference. The data indicated that the type and loading of UV stabilizer had no significant effect on the loss in flexural strength after exposed to sunlight for 4 months.



**Figure 5.12:** Change in flexural strength of PVC/TWF composites with and without UV stabilizer after exposed to sunlight

In Figure 5.12 the flexural strength of PVC/TWF composites without UV stabilizer decreased from 55.7 MPa to 40.4 MPa (approximately 27%) after exposed to sunlight for 4 months. PVC/TWF composites with 2 phr of XT stabilizer the flexural strength decreased from 55.5 MPa to 49.4 MPa (approximately 11%) after

exposure to sunlight. After exposed to sunlight up to 3 months, the flexural strength of PVC/TWF composites at various loadings of UV stabilizer showed little difference. For 4-month exposure, PVC/TWF composites with P and XT stabilizer at 1 phr showed small difference of flexural strength. However, the data also indicated that UV stabilizers had an effect on delaying the degradation from crosslinking or chain scission of polymer chain in composites and maintain flexural strength of PVC composites after exposure to sunlight. Moreover for 4-month exposure, the flexural strength of PVC/TWF composites decreased greater than that of PVC because wood flour undergoes photo-degradation, resulting in breakdown of lignin to form free radical. Which is consistent with the work of Nicole et al (2003). The free radicals may attack the polymer chain, due to the deleterious effect of the addition of wood flour to polymer through an accelerated chain scission in polymer as discussed in the work of Nicole et al [16]. Moreover, wood cell walls swell when exposed to water. The swelling of wood fiber in WPCs can cause microcracks between wood and matrix interface [18] resulting the higher loss in flexural strength of PVC/TWF composites.



**Figure 5.13:** Change in flexural strength of PVC/CC and PVC/TWF without UV stabilizer after exposed to sunlight

Figure 5.13 showed the changes in flexural strength of PVC/CC composites and PVC/TWF composites without UV stabilizer after exposed to sunlight. The flexural strength of PVC/TWF composites before weathering test was slightly higher than that of PVC/CC composite because teak wood flour contains more cellulose in the structures than that of corncob as shown in Table 5.1 [23]. The flexural strength of PVC/TWF composites without UV stabilizer decreased from 55.7 MPa to 40.4 MPa after exposed to sunlight for 4 months. That means the flexural strength decreased approximately 27%. PVC/CC composites without UV stabilizer decreased from 49.3 MPa to 37.5 MPa approximately 24% after exposed to sunlight for 4 months.

### **5.3.2 Flexural Modulus**

Sample	Flexural modulus (GPa) exposure time (month)				
	0	1	2	3	4
PVC	2.9	3.0	2.8	2.5	2.4
PVC+XT/1.0	3.0	3.0	2.8	2.8	2.8
PVC+XT/1.5	3.0	3.2	3.0	3.0	2.6
PVC+XT/2.0	2.9	2.9	<b>3</b> .1	3.1	2.8
PVC+P/2.0	2.9	3.0	2.7	2.7	2.8
PVC+CC	3.6	3.2	2.8	2.2	2.2
PVC/TWF	4.9	4.0	4.0	3.8	3.0
PVC/TWF+XT/1.0	5.7	5.3	4.9	4.2	3.3
PVC/TWF+XT/1.5	5.3	5.0	4.6	4.2	4.5
PVC/TWF+XT/2.0	4.9	5.1	3.8	3.8	4.3
PVC/TWF+P/2.0	5.2	4.6	5.0	4.9	4.3

**Table 5.2:** Change in flexural modulus of PVC and PVC composites

 with and without UV stabilizer after exposure to sunlight

Table 5.2 shows the change in flexural modulus of PVC and PVC/TWF composites with and without UV stabilizer after exposed to sunlight. The flexural modulus of PVC/CC composites and PVC/TWF composites was higher than that of PVC because CC and TWF are reinforcing fillers. The flexural modulus of PVC/TWF composites was higher than that of PVC/CC composites because the amount of cellulose of TWF was higher than that of CC. After exposed to sunlight the loss in flexural modulus of PVC without UV stabilizer were higher than that of PVC with UV stabilizer. The flexural modulus of PVC without UV stabilizer exhibited obvious loss after 2 months i.e. the flexural modulus decreased from 2.9 GPa to 2.4 GPa (about 17% decrease) after exposure to sunlight for 4 months. By adding of XT

stabilizer at the flexural modulus decreased from 2.9 GPa to 2.8 GPa after exposure to sunlight for 4 months which is only 3% decrease. In comparison between PVC with P and XT stabilizer at loading of 2 phr, their flexural modulus was slightly different after exposed to sunlight. The flexural modulus of PVC/TWF composites without UV stabilizer change from 4.9 GPa to 3.0 GPa (only 38% decrease), but the flexural modulus of PVC/TWF composites with XT stabilizer at 2.0 phr decreased from 5.1 GPa to 4.3 GPa (approximately 16% decrease). After 4 months, the values of flexural modulus of PVC/TWF composites with XT stabilizer at 1.5 phr and 2.0 phr were slightly different. Moreover, after exposure to sunlight for 4 months PVC/TWF composites with P and XT stabilizer at 2 phr showed a little difference of flexural modulus. The results indicated that UV stabilizers can delay the change in flexural modulus in both PVC and PVC composites but the types and loading of UV stabilizer had no significant effect on the flexural modulus. The flexural modulus of PVC composites decrease more than that of PVC after weathering because when wood exposure to water due to swelling of wood particles and can cause microcracks between wood and matrix interface the matrix. These results the loss of interfacial contribute the loss of stiffness of PVC composites [18]. The decrease of the flexural modulus of PVC/CC composites was slightly higher than that of PVC/TWF composites.

### **5.4 Tensile Property Analysis**



### 5.4.1 Tensile Strength

**Figure 5.14:** Change in tensile strength of PVC with and without UV stabilizer after exposed to sunlight

After exposed to sunlight for 4 months, the tensile strength of PVC without UV stabilizer was less than that of PVC with UV stabilizer as shown in Figure 5.14. After exposure to sunlight through 1 month, the tensile strength of PVC without UV stabilizer was slightly increased. During 1 to 4 months of exposure time, the tensile strength drastically decreased. At 4 months the change in tensile strength of PVC at 1.5 phr of XT stabilizer was slightly higher than that of PVC with 1.0 phr and 2.0 phr of XT stabilizer. PVC at 1.0 phr of XT stabilizer change in tensile strength showed
similar trend as that of 1.0 phr of P stabilizer after exposed to sunlight through 2 months. After 3 months of exposure time, the tensile strength of PVC with XT stabilizer was slightly increased but that with P stabilizer was slightly decreased. However, after 4 months PVC with P and XT stabilizer showed small difference of the tensile strength. The tensile strength of PVC without UV stabilizer decreased from 54.3 MPa to 48.2 MPa (approximately 11% decrease). PVC with 1 phr of XT stabilizer the tensile strength decreased from 53.7 MPa to 51.5 MPa (approximately 4% decrease). The data indicated that PVC with UV stabilizer showed greater tensile strength retention than PVC without UV stabilizer after exposure to sunlight. This phenomenon can be indicated by concentration carbonyl group as shown in Figure 5.3a).



**Figure 5.15:** Change in tensile strength of PVC/TWF composites with and without UV stabilizer after exposed to sunlight

Figure 5.15 shows the change in tensile strength of PVC/TWF composites with and without UV stabilizer after exposed to sunlight. The tensile strength of PVC/TWF composites without UV stabilizer decreased from 40.0 MPa to 26.2 MPa (approximately 34% decrease) after exposed to sunlight for 4 months. During 1 to 3 months of exposure time, PVC/TWF composites at various loadings of XT stabilizer showed a little difference of the tensile strength. However after 4 months, the change in flexural strength of PVC/TWF composites with 1.5 phr of XT stabilizer was slightly higher than the ones with 1.0 and 2.0 phr of UV stabilizer. In comparison between XT and P stabilizer at 1 phr for 4 months of exposure, the tensile strength of PVC/TWF composites with P and XT stabilizer decreased approximately 14% and

15% respectively. This result indicated that after exposed to sunlight for 4 months the decrease of the tensile strength of PVC/TWF composites without UV stabilizer was higher than that of PVC/TWF composites with UV stabilizer. The results can be proven by concentration carbonyl group as shown in Figure 5.3b) and supported by SEM micrographs as shown in Figure 5.16. SEM micrographs in Figure 5.16d) shows smaller amount of microcracks between filler and polymer matrix than Figure 5.16b). When determined only polymer matrix, SEM micrographs of PVC composites with UV stabilizer showed smaller size of microcrack than that of PVC composites without UV stabilizer because UV stabilizer can protect harmful effect from UV radiation and reduce the oxidation process. In addition, photo-oxidation can cause crosslinking and chain scission. The crosslinking may have hindered the chain mobility due to the increase in strength and modulus [16]. However, the occurrence of the crosslinking and the chain scission leads to the degradation of PVC and PVC composites.



**Figure 5.16:** SEM micrographs on surface of PVC/TWF composites a) PVC/TWF composites without UV stabilizer before exposure b) PVC/TWF composites without UV stabilizer after exposure c) PVC/TWF composites containing 1 phr of XT stabilizer before exposure d) PVC/TWF composites containing 1 phr of XT stabilizer after exposure



**Figure 5.17:** SEM micrographs on surface after weathering for 4 months of a) PVC/CC composites b) PVC/TWF composites



**Figure 5.18:** Change in tensile strength of PVC/CC composites and PVC/TWF composites without UV stabilizer after exposed to sunlight

Figure 5.18 shows the change in tensile strength of PVC/CC composites and PVC/TWF composites without UV stabilizer after exposed to sunlight. The tensile strength of PVC/TWF composites before weathering test was higher than that of PVC/CC composite because teak wood flour has cellulose in the structures more than corncob [22]. After exposed to sunlight for 4 months, the tensile strength of PVC/TWF composites without UV stabilizer decreased from 40.0 MPa to 26.2 MPa (approximately 34% decrease), whereas PVC/CC composites without UV stabilizer decreased from 33.7 MPa to 23.9 MPa (approximately 29% decrease). Therefore, the decrease of flexural strength occurred. The results can be supported by SEM micrograph as shown in Figure 5.17. PVC/CC composites showed smaller size of microcrack than PVC/TWF composites.

Sample	Tensile modulus (GPa) exposure time (months)				
	0	1	2	3	4
PVC	2.5	2.6	2.5	2.4	2.2
PVC+P/2.0	2.5	2.5	2.4	2.4	2.4
PVC+XT/1.0	2.4	2.4	2.3	2.5	2.5
PVC+XT/1.5	2.6	2.5	2.5	2.5	2.4
PVC+XT/2.0	2.4	2.5	2.5	2.6	2.5
PVC+CC	3.4	3.0	2.7	2.4	2.2
PVC/TWF	4.0	3.7	3.7	3.00	2.6
PVC/TWF+P/2.0	4.4	3.9	3.5	3.5	3.6
PVC/TWF+XT/1.0	4.3	4.00	3.6	3.7	3.8
PVC/TWF+XT/1.5	4.3	3.9	3.9	3.8	3.3
PVC/TWF+XT/2.0	4.3	3.6	3.9	3.8	3.4

 Table 5.3: Change in tensile modulus of PVC and PVC composites

 with and without UV stabilizers after exposure to sunlight

Table 5.3 shows the change in tensile modulus of PVC and PVC/TWF composites with and without UV stabilizers after exposure to sunlight. After exposure to sunlight for 4 months the tensile modulus of PVC without UV stabilizer decreased from 2.5 GPa to 2.2 GPa (approximately 12% decrease). PVC with XT stabilizer at 2.0 phr increased from 2.4 GPa to 2.5 GPa (approximately 4% increase). The trends of the change in tensile modulus of PVC with P and XT stabilizer at 2.0 phr were similar after exposure to sunlight. The results indicated that types and loadings of UV stabilizer had no significant effect on tensile modulus. The tensile modulus of PVC/TWF composites without UV stabilizer decreased from 4.0 GPa to 2.6 GPa (approximately 35% decrease). In comparison between PVC/TWF composites with P and XT stabilizer at 2.0 phr showed a small difference change in tensile modulus after

exposure to sunlight. The tensile modulus of PVCTWF composites with XT stabilizer at 2.0 phr decreased from 4.3 GPa to 3.4 GPa (approximately 21% decrease). The results indicated that types and loadings of UV stabilizer had no significant effect on tensile modulus, and UV stabilizer can delay the decrease of tensile modulus in both of PVC and PVC composites after exposure to sunlight. In comparison between PVC/TWF composites and PVC/CC composites, the decrease of the tensile modulus of PVC/CC composites was slightly higher than that of PVC/TWF composites.



#### **CHAPTER VI**

1

#### **CONCLUSIONS**

In this study, the effect of UV stabilizer types and loadings on PVC/TWF composites and PVC/CC composites were examined by the changes in their appearance and mechanical properties before and after natural weathering test for 4 months. The color change and mechanical properties of samples were determined every week and every month, respectively. The measurement consisted of surface chemical change, color change, tensile and flexural properties.

After weathering test PVC and PVC composites without UV stabilizer showed a higher concentration of carbonyl group more than that of PVC and PVC composites with UV stabilizer. Moreover, PVC composites showed a higher concentration of carbonyl group more than that of PVC. UV stabilizer can reduce the oxidation process but type and loading of UV stabilizer dose not significantly affect the concentration of carbonyl group.

UV stabilizer can delay the color change of PVC but not delay the color change of PVC composite. PVC/TWF composites with a higher  $TiO_2$  showed the smaller lightness change. Moreover, color of PVC/TWF composites change more than that of PVC/CC composites.

In addition, after weathering test the change in tensile and the flexural strength of PVC/TWF composites without UV stabilizer showed a slightly higher than that of PVC/CC composites without UV stabilizer. On the other hand, the change in tensile modulus and the flexural modulus of PVC/CC composites without UV stabilizer were a slightly higher than those of PVC/TWF composites without UV stabilizer.

UV stabilizer can maintain the tensile and flexural properties of PVC and PVC composites after weathering test. The type and loading of UV stabilizer did not significant effect on color change and mechanical properties.

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# ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

APPENDICES

### Appendix A

### **Color Change of PVC and PVC Composites**

The total difference  $dE_{ab}^*$  between two colors each given in terms of lightness (L\*) and chromaticity coordinate ( a\* and b\*) is calculated following ASTM D 2244 by Ultrascan pro in CIE color system.

$$dE^* = [(dL^*)^2 + (da^*)^2 + (db^*)^2]^{1/2}$$

 $dL^* = L_1^* - L_0^*$  $da^* = a_1^* - a_0^*$  $db^* = b_1^* - b_0^*$ 

Where  $L_0^*$ ,  $a_0^*$  and  $b_0^*$  refer to the initial, and  $L_1^*$ ,  $a_1^*$  and  $b_1^*$  refer to the final specimen. The signs of the components dL<sup>\*</sup>, da<sup>\*</sup> and db<sup>\*</sup> have the following approximate meanings;

```
+dL* = lighter

-dL* = darker

+da* = redder (less green)

-da* = greener (less red)

+db* = yellow (less blue)

-db* = bluer (less yellow)
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จุฬาลงกรณ์มหาวิทยาลัย

Samples	dL*	da*	db*	dE*
PVC	-7.7±0.1	0.2±0.0	-3.6±0.2	8.5±0.1
PVC+P/1.0	0.4±0.1	0.1±0.0	-1.8±0.1	1.8±0.1
PVC+P/1.5	0.5±0.1	0.1±0.0	-2.0±0.2	2.0±0.2
PVC+P/2.0	0.7±0.2	0.2±0.0	-2.3±0.2	2.4±0.2
PVC+XT/1.0	0.5±0.1	0.0±0.0	-1.4±0.1	1.5±0.2
PVC+XT/1.5	0.5±0.1	-0.0±0.0	-1.5±0.1	1.6±0.1
PVC+XT/2.0	0.5±0.1	-0.1±0.1	-1.4±0.2	1.5±0.3
PVC/CC	1.3±0.1	-1.6±0.1	-3.5±0.2	4.1±0.2
PVC/CC+P/1.0	2.2±0.3	-2.0±0.1	-3.6±0.1	4.7±0.2
PVC/CC+P/1.5	2.7±0.4	-2.1±0.2	-4.1±0.2	5.3±0.3
PVC/CC+P/2.0	2.8±0.6	-2.0±0.1	-3.9±0.2	5.2±0.5
PVC/CC+XT/1.0	2.2±0.1	-1.8±0.2	-3.0±0.2	4.2±0.2
PVC/CC+XT/1.5	2.2±0.7	-1.8±0.1	-3.1±0.4	4.2±0.1
PVC/CC+XT/2.0	1.7±0.2	-1.7±0.1	-3.1±0.1	3.4±0.2
PVC/TWF	1.7±0.0	-0.6±0.0	1.0±0.1	2.0±0.0
PVC/TWF+Ti1/5	3.0±0.2	-0.7±0.0	-1.7±0.1	3.5±0.2
PVC/TWF+Ti1/10	3.0±0.2	-0.7±0.0	-1.9±0.1	3.7±0.2
PVC/TWF+Ti1/15	3.2±0.2	-0.6±0.0	-1.5±0.1	3.6±0.2
PVC/TWF+Ti2/5	3.0±0.2	-0.5±0.1	-2.2±0.1	3.7±0.1
PVC/TWF+Ti2/10	3.4±0.2	-0.5±0.0	-2.1±0.1	4.0±0.1
PVC/TWF+Ti2/15	3.6±0.1	-0.7±0.0	-1.6±0.1	4.0±0.1
PVC/TWF+P/1.0	1.4±0.4	-0.5±0.0	0.6±0.1	1.6±0.4
PVC/TWF+P/1.5	1.0±0.5	-0.5±0.1	-0.1±0.4	1.2±0.3
PVC/TWF+P/2.0	1.8±0.3	-0.5±0.1	0.6±0.1	2.0±0.3
PVC/TWF+XT/1.0	2.0±0.2	-0.3±0.1	0.9±0.1	2.2±0.2
PVC/TWF+XT/1.5	1.5±0.0	-0.5±0.1	0.8±0.2	1.8±0.1
PVC/TWF+XT/2.0	1.2±0.2	-0.4±0.1	0.6±0.4	1.4±0.2

Appendix A-1 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 1 week.

Sample	dL*	da*	db*	dE*
PVC	-9.5±0.4	-0.3±0.0	-5.3±0.4	10.8±0.2
PVC+P/1.0	0.3±0.1	-0.0±0.0	-2.1±0.1	2.1±0.1
PVC+P/1.5	0.5±0.1	-0.0±0.0	-2.3±0.1	2.4±0.1
PVC+P/2.0	0.5±0.3	0.1±0.0	-2.7±0.2	2.7±0.3
PVC+XT/1.0	0.5±0.1	-0.2±0.0	-1.8±0.1	1.9±0.1
PVC+XT/1.5	0.6±0.1	-0.2±0.0	-2.1±0.2	2.2±0.2
PVC+XT/2.0	0.6±0.0	-0.2±0.1	-2.0±0.0	2.1±0.0
PVC/CC	2.2±0.2	-1.9±0.1	-4.0±0.1	4.7±0.2
PVC/CC+P/1.0	4.2±0.4	-2.8±0.1	-4.3±0.2	6.6±0.4
PVC/CC+P/1.5	4.4±0.4	-3.0±0.1	-4.7±0.3	7.0±0.5
PVC/CC+P/2.0	4.0±1.0	-2.7±0.2	-4.6±0.3	6.7±0.8
PVC/CC+XT/1.0	4.0±0.5	-2.5±0.2	-3.6±0.3	5.9±0.5
PVC/CC+XT/1.5	3.9±0.4	-2.6±0.1	-3.9±0.1	6.1±0.2
PVC/CC+XT/2.0	4.1±0.5	-2.8±0.1	-4.4±0.1	6.6±0.4
PVC/TWF	4.4±0.4	-0.3±0.1	1.7±0.3	4.8±0.4
PVC/TWF+Ti1/5	5.5±0.2	-0.6±0.1	-1.4±0.1	5.7±0.2
PVC/TWF+Ti1/10	5.3±0.4	-0.6±0.1	-1.6±0.1	5.5±0.3
PVC/TWF+Ti1/15	4.5±0.1	-0.6±0.0	-1.3±0.1	4.7±0.1
PVC/TWF+Ti2/5	5.1±0.5	-0.3±0.1	-1.6±0.2	5.4±0.4
PVC/TWF+Ti2/10	5.0±0.1	-0.4±0.0	-1.5±0.0	5.2±0.1
PVC/TWF+Ti2/15	5.0±0.4	-0.5±0.1	-0.9±0.1	5.1±0.3
PVC/TWF+P/1.0	4.7±0.2	-0.3±0.2	2.2±0.4	5.2±0.1
PVC/TWF+P/1.5	3.6±0.2	-0.1±0.1	1.7±0.4	4.0±0.4
PVC/TWF+P/2.0	3.3±0.4	-0.4±0.2	1.5±0.4	3.7±0.5
PVC/TWF+XT/1.0	4.1±0.3	0.0±0.1	2.6±0.2	4.8±0.2
PVC/TWF+XT/1.5	4.0±0.5	-0.2±0.1	2.3±0.4	4.6±0.6
PVC/TWF+XT/2.0	4.3±0.5	-0.3±0.1	2.0±0.1	4.7±0.5

**Appendix A-2** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 2 weeks.

Sample	dL*	da*	db*	dE*
PVC	-9.9±0.1	-0.5±0.1	-5.9±0.2	11.5±0.1
PVC+P/1.0	0.3±0.2	0.0±0.0	-2.1±0.2	2.1±0.2
PVC+P/1.5	0.5±0.1	-0.0±0.0	-2.3±0.1	2.4±0.1
PVC+P/2.0	0.2±0.5	0.1±0.1	-2.6±0.1	2.6±0.2
PVC+XT/1.0	0.5±0.1	-0.2±0.0	-1.9±0.1	2.0±0.1
PVC+XT/1.5	0.5±0.2	-0.2±0.0	-2.0±0.2	2.1±0.2
PVC+XT/2.0	0.7±0.1	-0.3±0.1	-1.8±0.2	2.0±0.2
PVC/CC	2.3±0.1	-1.8±0.1	-3.8±0.2	4.8±0.3
PVC/CC+P/1.0	5.0±0.1	-2.7±0.1	-3.8±0.1	6.8±0.1
PVC/CC+P/1.5	4.7±0.1	-2.8±0.1	-4.2±0.4	6.8±0.2
PVC/CC+P/2.0	5.2±0.6	-2.8±0.1	-4.1±0.2	7.2±0.5
PVC/CC+XT/1.0	5.1±0.6	-2.7±0.1	-3.2±0.3	6.6±0.4
PVC/CC+XT/1.5	4.3±0.8	-2.7±0.1	-3.4±0.5	6.1±0.4
PVC/CC+XT/2.0	5.8±0.1	-2.8±0.0	-3.3±0.2	7.2±0.0
PVC/TWF	7.3±0.3	-0.2±0.1	2.1±0.2	7.6±0.3
PVC/TWF+Ti1/5	7.3±0.4	-0.3±0.1	-0.5±0.1	7.3±0.4
PVC/TWF+Ti1/10	6.2±0.1	-0.4±0.0	-0.8±0.1	6.2±0.1
PVC/TWF+Ti1/15	5.2±0.3	-0.3±0.1	-0.7±0.1	5.2±0.3
PVC/TWF+Ti2/5	6.3±0.3	-0.1±0.1	-0.7±0.2	6.3±0.3
PVC/TWF+Ti2/10	5.8±0.1	-0.1±0.1	-0.4±0.2	5.8±0.1
PVC/TWF+Ti2/15	5.7±0.1	-0.2±0.1	-0.1±0.2	5.7±0.1
PVC/TWF+P/1.0	6.3±0.6	-0.3±0.1	2.6±0.3	6.8±0.7
PVC/TWF+P/1.5	5.3±0.4	-0.4±0.1	1.8±0.3	5.6±0.5
PVC/TWF+P/2.0	6.1±0.3	-0.2±0.2	3.0±0.5	6.8±0.4
PVC/TWF+XT/1.0	6.7±0.4	0.2±0.1	3.8±0.2	7.7±0.4
PVC/TWF+XT/1.5	6.2±0.4	0.1±0.1	3.7±0.3	7.2±0.5
PVC/TWF+XT/2.0	6.3±0.3	0.1±0.1	3.4±0.2	7.1±0.3

**Appendix A-3** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 3 weeks.

Sample	dL*	da*	db*	dE*
PVC	-11.6±0.6	-0.5±0.1	-5.6±0.5	12.9±0.3
PVC+P/1.0	0.1±0.1	0.0±0.1	-2.2±0.1	2.2±0.1
PVC+P/1.5	0.3±0.1	0.0±0.0	-2.5±0.1	2.5±0.1
PVC+P/2.0	0.2±0.1	0.1±0.0	-2.7±0.1	2.8±0.1
PVC+XT/1.0	0.3±0.1	-0.1±0.0	-2.0±0.0	2.0±0.0
PVC+XT/1.5	0.2±0.1	-0.1±0.0	-1.9±0.1	1.9±0.1
PVC+XT/2.0	0.4±0.1	-0.2±0.1	1.7±0.1	1.8±0.1
PVC/CC	4.7±0.2	-2.8±0.1	-8.8±0.2	10.3±0.2
PVC/CC+P/1.0	7.9±0.5	-3.7±0.1	-7.5±0.3	11.6±0.2
PVC/CC+P/1.5	8.4±0.4	-3.8±0.0	-8.1±0.1	12.3±0.2
PVC/CC+P/2.0	8.3±0.2	-3.8±0.0	-7.7±0.2	12.0±0.2
PVC/CC+XT/1.0	8.0±0.1	-3.7±0.1	-6.6±0.1	11.0±0.1
PVC/CC+XT/1.5	7.9±0.6	-3.7±0.1	-6.7±0.4	11.1±0.2
PVC/CC+XT/2.0	9.0±0.2	-4.2±0.1	-7.8±0.2	12.6±0.1
PVC/TWF	16.1±0.4	-0.5±0.2	2.5±0.3	16.3±0.4
PVC/TWF+Ti1/5	9.1±0.2	-0.3±0.0	-0.3±0.0	9.1±0.2
PVC/TWF+Ti1/10	7.0±0.1	-0.2±0.0	-0.6±0.1	7.1±0.2
PVC/TWF+Ti1/15	5.9±0.4	-0.3±0.0	-0.6±0.2	5.9±0.4
PVC/TWF+Ti2/5	8.7±0.3	0.1±0.1	0.1±0.2	8.7±0.3
PVC/TWF+Ti2/10	7.1±0.0	0.1±0.1	0.1±0.3	7.2±0.0
PVC/TWF+Ti2/15	5.9±0.2	-0.1±0.0	0.4±0.1	5.9±0.2
PVC/TWF+P/1.0	15.2±0.5	-0.4±0.1	3.7±0.2	15.6±0.5
PVC/TWF+P/1.5	14.6±0.0	-0.4±0.1	3.7±0.3	15.0±0.1
PVC/TWF+P/2.0	14.9±0.3	-0.4±0.1	4.3±0.2	15.5±0.3
PVC/TWF+XT/1.0	14.3±0.9	-0.2±0.1	4.1±0.3	14.8±1.0
PVC/TWF+XT/1.5	15.2±0.4	-0.5±0.1	4.3±0.3	15.8±0.4
PVC/TWF+XT/2.0	13.7±0.5	0.0±0.0	4.7±0.2	14.5±0.5

**Appendix A-4** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 4 weeks.

Sample	dL*	da*	db*	dE*
PVC	-12.3±0.2	-0.5±0.1	-5.2±0.1	13.3±0.2
PVC+P/1.0	-0.2±0.1	0.0±0.0	-2.1±0.1	2.1±0.1
PVC+P/1.5	-0.2±0.2	0.0±0.0	-2.4±0.1	2.4±0.1
PVC+P/2.0	-0.1±0.6	0.1±0.1	-2.8±0.3	2.8±0.3
PVC+XT/1.0	0.3±0.1	-0.0±0.0	-2.0±0.0	2.0±0.0
PVC+XT/1.5	0.0±0.1	-0.0±0.0	-1.9±0.1	1.9±0.1
PVC+XT/2.0	0.0±0.3	-0.2±0.1	-1.8±0.2	1.9±0.2
PVC/CC	5.1±0.3	-3.0±0.1	-11.1±0.2	12.6±0.3
PVC/CC+P/1.0	7.4±0.1	-3.4±0.1	-6.2±0.3	10.2±0.2
PVC/CC+P/1.5	7.4±0.1	-3.3±0.1	-6.4±0.4	10.3±0.4
PVC/CC+P/2.0	7.6±0.4	-3.5±0.0	-6.5±0.2	10.6±0.4
PVC/CC+XT/1.0	7.8±0.2	-3.5±0.0	-5.4±0.1	10.1±0.2
PVC/CC+XT/1.5	7.1±0.4	-3.5±0.1	-5.8±0.2	9.8±0.3
PVC/CC+XT/2.0	8.4±0.4	-3.5±0.1	-5.4±0.1	10.6±0.4
PVC/TWF	17.2±0.2	-0.5±0.0	2.4±0.1	17.4±0.2
PVC/TWF+Ti1/5	9.8±0.2	0.1±0.1	0.2±0.1	9.8±0.2
PVC/TWF+Ti1/10	7.7±0.1	0.1±0.0	-0.4±0.1	7.7±0.1
PVC/TWF+Ti1/15	6.4±0.3	-0.1±0.0	-0.4±0.1	6.4±0.3
PVC/TWF+Ti2/5	9.6±0.1	0.6±0.0	1.2±0.1	9.7±0.1
PVC/TWF+Ti2/10	7.8±0.2	0.5±0.1	0.8±0.2	7.9±0.2
PVC/TWF+Ti2/15	6.6±0.1	0.3±0.0	0.8±0.1	6.7±0.1
PVC/TWF+P/1.0	16.1±0.1	-0.2±0.1	4.2±0.2	16.7±0.1
PVC/TWF+P/1.5	15.9±0.2	-0.1±0.0	4.6±0.1	16.5±0.2
PVC/TWF+P/2.0	15.4±0.1	0.0±0.1	5.4±0.2	16.3±0.2
PVC/TWF+XT/1.0	15.8±0.3	0.1±0.1	4.7±0.2	16.5±0.3
PVC/TWF+XT/1.5	15.6±0.2	-0.0±0.3	4.9±0.5	16.4±0.1
PVC/TWF+XT/2.0	14.8±0.3	0.3±0.1	5.2±0.2	15.7±0.4

**Appendix A-5** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 5 weeks.

Sample	dL*	da*	db*	dE*
PVC	-13.1±0.6	-0.5±0.0	-4.9±0.4	14.0±0.5
PVC+P/1.0	-0.0±0.1	0.1±0.0	-2.3±0.0	2.3±0.0
PVC+P/1.5	0.1±0.1	0.1±0.0	-2.4±0.0	2.4±0.0
PVC+P/2.0	0.4±0.1	0.2±0.1	-2.9±0.1	2.9±0.1
PVC+XT/1.0	0.1±0.0	-0.1±0.0	-2.0±0.1	2.0±0.1
PVC+XT/1.5	0.1±0.2	-0.1±0.0	-2.0±0.2	2.1±0.2
PVC+XT/2.0	0.3±0.1	-0.1±0.0	-1.7±0.1	1.8±0.1
PVC/CC	5.5±0.3	-3.4±0.1	-11.3±0.2	13.1±0.3
PVC/CC+P/1.0	8.4±0.2	-3.8±0.1	-7.8±0.0	12.1±0.1
PVC/CC+P/1.5	8.5±0.3	-3.8±0.1	7.9±0.1	12.2±0.2
PVC/CC+P/2.0	8.4±0.3	-3.9±0.1	-7.6±0.1	12.0±0.3
PVC/CC+XT/1.0	8.6±0.4	-3.9±0.0	-7.0±0.1	11.8±0.3
PVC/CC+XT/1.5	8.5±0.6	-3.8±0.1	-6.7±0.1	11.5±0.5
PVC/CC+XT/2.0	9.1±0.1	-4.1±0.1	-7.4±0.2	12.4±0.1
PVC/TWF	18.7±0.2	-0.7±0.1	2.4±0.4	18.9±0.2
PVC/TWF+Ti1/5	10.3±0.4	-0.2±0.1	0.0±0.1	10.3±0.4
PVC/TWF+Ti1/10	8.0±0.1	-0.1±0.0	-0.4±0.1	8.0±0.1
PVC/TWF+Ti1/15	6.7±0.1	-0.1±0.1	-0.4±0.1	6.7±0.1
PVC/TWF+Ti2/5	10.1±0.1	0.2±0.1	0.7±0.3	10.1±0.1
PVC/TWF+Ti2/10	8.2±0.0	0.3±0.1	0.6±0.3	8.2±0.0
PVC/TWF+Ti2/15	6.9±0.1	0.0±0.1	0.6±0.1	6.9±0.1
PVC/TWF+P/1.0	17.9±0.4	-0.6±0.1	4.0±0.2	18.4±0.4
PVC/TWF+P/1.5	16.8±0.3	-0.5±0.1	4.2±0.0	17.3±0.3
PVC/TWF+P/2.0	16.2±0.4	-0.5±0.1	4.4±0.3	16.8±0.5
PVC/TWF+XT/1.0	16.8±0.3	-0.1±0.1	4.5±0.2	17.4±0.3
PVC/TWF+XT/1.5	17.5±0.4	-0.4±0.1	4.8±0.1	18.2±0.4
PVC/TWF+XT/2.0	16.1±0.5	-0.1±0.0	4.9±0.1	16.8±0.5

**Appendix A-6** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 6 weeks.

Sample	dL*	da*	db*	dE*
PVC	-13.6±0.2	-0.5±0.0	-4.9±0.4	14.5±0.1
PVC+P/1.0	-0.1±0.0	-0.0±0.0	-2.3±0.0	2.3±0.0
PVC+P/1.5	-0.0±0.1	-0.0±0.0	-2.3±0.1	2.3±0.1
PVC+P/2.0	0.3±0.2	0.1±0.0	-2.9±0.2	2.9±0.2
PVC+XT/1.0	0.1±0.2	-0.1±0.1	-2.0±0.1	2.0±0.1
PVC+XT/1.5	-0.0±0.3	-0.0±0.0	-2.1±0.2	2.1±0.2
PVC+XT/2.0	0.2±0.1	-0.1±0.1	-1.9±0.2	1.9±0.2
PVC/CC	7.7±0.5	-3.6±0.0	-13.2±0.0	15.7±0.3
PVC/CC+P/1.0	8.7±0.1	-3.7±0.0	-8.2±0.1	12.5±0.1
PVC/CC+P/1.5	8.6±0.1	-3.8±0.1	-8.5±0.0	12.7±0.1
PVC/CC+P/2.0	8.9±0.2	-3.8±0.1	-8.1±0.2	12.6±0.2
PVC/CC+XT/1.0	8.9±0.3	-3.8±0.0	-7.1±0.1	12.0±0.2
PVC/CC+XT/1.5	8.5±0.3	-3.7±0.1	-7.1±0.2	11.6±0.3
PVC/CC+XT/2.0	9.8±0.3	-3.8±0.0	-7.0±0.1	12.6±0.2
PVC/TWF	21.5±0.1	-0.5±0.1	3.2±0.1	21.8±0.1
PVC/TWF+Ti1/5	11.1±0.2	-0.1±0.0	0.3±0.0	11.1±0.2
PVC/TWF+Ti1/10	8.2±0.0	-0.1±0.0	-0.3±0.1	8.2±0.0
PVC/TWF+Ti1/15	6.7±0.2	-0.2±0.0	-0.2±0.1	6.8±0.2
PVC/TWF+Ti2/5	10.7±0.1	0.5±0.1	1.6±0.2	10.8±0.1
PVC/TWF+Ti2/10	8.6±0.3	0.4±0.1	1.1±0.1	8.6±0.3
PVC/TWF+Ti2/15	7.2±0.1	0.2±0.1	0.9±0.1	7.2±0.1
PVC/TWF+P/1.0	21.1±0.1	-0.4±0.1	4.5±0.1	21.6±0.1
PVC/TWF+P/1.5	20.5±0.2	-0.3±0.1	4.9±0.1	21.1±0.2
PVC/TWF+P/2.0	20.5±0.1	-0.1±0.1	5.8±0.1	21.3±0.1
PVC/TWF+XT/1.0	20.6±0.1	0.1±0.1	4.8±0.2	21.1±0.2
PVC/TWF+XT/1.5	20.2±0.2	-0.3±0.2	5.0±0.2	20.8±0.2
PVC/TWF+XT/2.0	19.6±0.4	0.1±0.1	5.7±0.3	20.4±0.5

**Appendix A-7** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 7 weeks.

Sample	dL*	da*	db*	dE*
PVC	-13.9±0.1	-0.4±0.0	-4.6±0.0	14.7±0.1
PVC+P/1.0	-0.2±0.1	0.0±0.1	-2.2±0.0	2.2±0.0
PVC+P/1.5	-0.2±0.2	-0.0±0.0	-2.2±0.0	2.2±0.0
PVC+P/2.0	-0.4±0.2	0.2±0.0	-2.6±0.1	2.7±0.1
PVC+XT/1.0	0.1±0.2	-0.1±0.0	-2.0±0.0	2.1±0.0
PVC+XT/1.5	-0.3±0.2	-0.0±0.1	-2.0±0.1	2.0±0.0
PVC+XT/2.0	0.0±0.1	-0.2±0.0	-1.7±0.1	1.8±0.1
PVC/CC	7.5±0.2	-3.7±0.0	-13.5±0.2	15.9±0.1
PVC/CC+P/1.0	8.0±0.3	-3.3±0.0	-8.3±0.0	12.0±0.2
PVC/CC+P/1.5	7.7±0.1	-3.3±0.1	-8.4±0.1	11.9±0.2
PVC/CC+P/2.0	7.9±0.1	-3.4±0.0	-7.7±0.1	11.6±0.1
PVC/CC+XT/1.0	8.1±0.1	-3.5±0.1	-7.6±0.2	11.6±0.1
PVC/CC+XT/1.5	7.9±0.4	-3.4±0.1	-6.8±0.3	11.0±0.2
PVC/CC+XT/2.0	8.1±0.2	-3.5±0.0	-6.9±0.1	11.2±0.2
PVC/TWF	22.6±0.1	-0.6±0.0	3.5±0.2	22.9±0.1
PVC/TWF+Ti1/5	10.3±0.1	-0.1±0.0	0.6±0.3	10.4±0.1
PVC/TWF+Ti1/10	7.3±0.1	-0.1±0.0	0.4±0.1	7.4±0.1
PVC/TWF+Ti1/15	5.3±0.2	-0.2±0.0	0.9±0.1	5.4±0.2
PVC/TWF+Ti2/5	10.3±0.1	0.5±0.0	2.8±0.3	10.7±0.0
PVC/TWF+Ti2/10	7.3±0.1	0.5±0.1	2.5±0.2	7.7±0.1
PVC/TWF+Ti2/15	6.2±0.1	0.2±0.1	1.8±0.1	6.4±0.1
PVC/TWF+P/1.0	22.2±0.0	-0.4±0.0	4.6±0.2	22.7±0.1
PVC/TWF+P/1.5	21.9±0.1	-0.1±0.2	5.6±0.6	22.6±0.1
PVC/TWF+P/2.0	21.4±0.1	-0.1±0.1	5.8±0.1	22.1±0.1
PVC/TWF+XT/1.0	21.9±0.1	-0.1±0.1	4.7±0.3	22.4±0.1
PVC/TWF+XT/1.5	21.5±0.2	-0.4±0.1	4.9±0.1	22.0±0.2
PVC/TWF+XT/2.0	20.8±0.1	0.1±0.1	5.8±0.1	21.6±0.1

**Appendix A-8** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 8 weeks.

Sample	dL*	da*	db*	dE*
PVC	-13.8±0.1	-0.5±0.0	-4.9±0.2	14.7±0.1
PVC+P/1.0	-0.5±0.2	-0.0±0.1	-2.0±0.1	2.1±0.0
PVC+P/1.5	-0.6±0.1	0.0±0.0	-2.0±0.1	2.1±0.0
PVC+P/2.0	-0.2±0.1	0.1±0.0	-2.7±0.0	2.7±0.0
PVC+XT/1.0	-0.1±0.2	-0.1±0.0	-1.9±0.2	1.9±0.2
PVC+XT/1.5	-0.4±0.3	-0.0±0.0	-1.9±0.1	1.9±0.1
PVC+XT/2.0	-0.5±0.2	-0.1±0.0	-1.5±0.1	1.6±0.1
PVC/CC	8.2±0.1	-3.7±0.1	-14.2±0.2	16.8±0.2
PVC/CC+P/1.0	8.7±0.2	-3.7±0.0	-8.6±0.0	12.7±0.1
PVC/CC+P/1.5	8.4±0.2	-3.8±0.0	-8.7±0.2	12.7±0.0
PVC/CC+P/2.0	8.3±0.2	-3.8±0.0	-8.6±0.0	12.6±0.1
PVC/CC+XT/1.0	9.1±0.3	-3.8±0.0	-7.4±0.1	12.3±0.1
PVC/CC+XT/1.5	8.1±0.2	-3.8±0.1	-7.6±0.1	11.7±0.1
PVC/CC+XT/2.0	9.2±0.3	-3.9±0.1	-7.6±0.1	12.5±0.1
PVC/TWF	23.6±0.2	-1.0±0.1	2.4±0.2	23.7±0.1
PVC/TWF+Ti1/5	11.7±0.3	-0.2±0.0	-0.2±0.1	11.7±0.3
PVC/TWF+Ti1/10	8.8±0.5	-0.2±0.0	-0.9±0.3	8.9±0.5
PVC/TWF+Ti1/15	7.2±0.2	-0.3±0.0	-0.7±0.1	7.2±0.2
PVC/TWF+Ti2/5	11.4±0.1	0.5±0.1	1.9±0.3	11.6±0.1
PVC/TWF+Ti2/10	8.1±0.1	0.6±0.1	1.7±0.1	8.2±0.1
PVC/TWF+Ti2/15	7.0±0.1	0.2±0.0	1.1±0.1	7.1±0.1
PVC/TWF+P/1.0	22.7±0.3	-0.4±0.0	3.9±0.0	23.0±0.3
PVC/TWF+P/1.5	22.3±0.2	-0.4±0.0	4.4±0.2	22.7±0.1
PVC/TWF+P/2.0	21.8±0.1	0.0±0.1	5.8±0.2	22.6±0.1
PVC/TWF+XT/1.0	22.7±0.2	-0.4±0.2	3.6±0.4	23.0±0.2
PVC/TWF+XT/1.5	22.3±0.1	-0.6±0.1	4.1±0.1	22.6±0.1
PVC/TWF+XT/2.0	21.2±0.3	0.1±0.1	5.6±0.0	21.9±0.3

**Appendix A-9** The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 9 weeks.

Sample	dL*	da*	db*	dE*
PVC	-14.7±0.5	-0.3±0.0	-4.0±0.2	15.3±0.4
PVC+P/1.0	-1.3±0.3	0.1±0.1	-1.7±0.2	2.2±0.1
PVC+P/1.5	-1.0±0.2	0.1±0.0	-1.9±0.1	2.1±0.0
PVC+P/2.0	-0.4±0.1	0.1±0.0	-2.5±0.0	2.6±0.0
PVC+XT/1.0	-1.3±0.2	0.1±0.1	-1.5±0.1	2.0±0.1
PVC+XT/1.5	-0.5±0.2	0.0±0.0	-1.9±0.1	1.9±0.1
PVC+XT/2.0	-0.5±0.2	-0.1±0.0	-1.6±0.1	1.7±0.1
PVC/CC	9.1±0.4	-4.0±0.0	-15.2±0.0	18.1±0.2
PVC/CC+P/1.0	8.5±0.2	-3.4±0.1	-9.3±0.2	13.1±0.2
PVC/CC+P/1.5	7.9±0.2	-3.4±0.0	-9.3±0.0	12.6±0.1
PVC/CC+P/2.0	8.0±0.1	-3.5±0.1	-9.0±0.1	12.5±0.1
PVC/CC+XT/1.0	9.2±0.2	-3.8±0.0	-8.9±0.1	13.3±0.1
PVC/CC+XT/1.5	8.3±0.6	-3.5±0.0	-7.9±0.3	12.0±0.2
PVC/CC+XT/2.0	9.7±0.3	-3.8±0.1	-8.3±0.3	13.3±0.1
PVC/TWF	28.2±0.1	-2.0±0.0	0.4±0.1	28.3±0.1
PVC/TWF+Ti1/5	13.7±0.1	-0.8±0.0	-2.1±0.1	13.9±0.1
PVC/TWF+Ti1/10	9.9±0.1	-0.6±0.0	-2.5±0.0	10.2±0.1
PVC/TWF+Ti1/15	8.1±0.1	-0.6±0.0	-2.3±0.6	8.5±0.1
PVC/TWF+Ti2/5	13.3±0.1	$0.0\pm0.0$	0.5±0.0	13.3±0.1
PVC/TWF+Ti2/10	9.7±0.1	0.1±0.0	0.1±0.1	9.7±0.1
PVC/TWF+Ti2/15	8.2±0.0	-0.2±0.0	0.0±0.1	8.2±0.1
PVC/TWF+P/1.0	27.6±0.1	-1.1±0.2	2.9±0.4	27.8±0.1
PVC/TWF+P/1.5	27.2±0.2	-0.9±0.0	4.0±0.1	27.5±0.2
PVC/TWF+P/2.0	26.9±0.3	-0.8±0.1	4.4±0.3	27.2±0.2
PVC/TWF+XT/1.0	27.3±0.1	-1.0±0.0	2.6±0.1	27.5±0.1
PVC/TWF+XT/1.5	26.5±0.1	-1.4±0.1	2.4±0.3	26.6±0.1
PVC/TWF+XT/2.0	26.1±0.1	-0.8±0.2	3.9±0.3	26.4±0.1

Appendix A-10 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 10 weeks.

Sample	dL*	da*	db*	dE*
PVC	-15.2±0.1	-0.1±0.1	-3.0±0.4	15.5±0.0
PVC+P/1.0	-1.4±0.2	0.1±0.1	-1.8±0.1	2.3±0.1
PVC+P/1.5	-0.9±0.1	0.1±0.0	-2.0±0.0	2.3±0.0
PVC+P/2.0	-1.1±0.4	0.2±0.1	-2.5±0.1	2.7±0.1
PVC+XT/1.0	-1.2±0.2	0.1±0.0	-1.6±0.0	2.1±0.1
PVC+XT/1.5	-1.2±0.4	0.1±0.1	-1.7±0.1	2.1±0.1
PVC+XT/2.0	-0.9±0.1	0.0±0.0	-1.6±0.0	1.8±0.1
PVC/CC	9.3±0.2	-4.1±0.1	-15.5±0.2	18.5±0.2
PVC/CC+P/1.0	8.5±0.3	-3.4±0.1	-9.7±0.2	13.3±0.3
PVC/CC+P/1.5	7.9±0.2	-3.3±0.1	-9.5±0.1	12.7±0.2
PVC/CC+P/2.0	7.8±0.3	-3.4±0.1	-9.2±0.2	12.6±0.2
PVC/CC+XT/1.0	9.9±0.6	-3.8±0.1	-9.2±0.1	14.0±0.4
PVC/CC+XT/1.5	8.4±0.6	-3.5±0.1	-8.1±0.3	12.2±0.2
PVC/CC+XT/2.0	8.8±0.0	-3.7±0.1	-8.5±0.4	12.8±0.3
PVC/TWF	29.5±0.2	-2.4±0.1	0.1±0.3	29.6±0.2
PVC/TWF+Ti1/5	14.2±0.1	-0.9±0.0	-2.4±0.1	14.4±0.1
PVC/TWF+Ti1/10	10.3±0.1	-0.7±0.0	-3.0±0.0	10.8±0.1
PVC/TWF+Ti1/15	8.2±0.5	-0.7±0.0	-2.6±0.2	8.7±0.5
PVC/TWF+Ti2/5	13.8±0.1	-0.2±0.0	0.3±0.1	13.8±0.1
PVC/TWF+Ti2/10	9.9±0.1	-0.1±0.0	0.1±0.0	9.9±0.1
PVC/TWF+Ti2/15	7.9±0.4	-0.2±0.0	0.1±0.1	7.9±0.4
PVC/TWF+P/1.0	28.7±0.3	-1.4±0.0	2.2±0.1	28.8±0.3
PVC/TWF+P/1.5	28.4±0.4	-1.2±0.1	3.2±0.0	28.6±0.4
PVC/TWF+P/2.0	28.0±0.4	-1.1±0.0	3.7±0.1	28.2±0.4
PVC/TWF+XT/1.0	29.0±0.2	-1.4±0.1	1.8±0.2	29.1±0.2
PVC/TWF+XT/1.5	28.1±0.4	-1.9±0.1	1.2±0.1	28.2±0.4
PVC/TWF+XT/2.0	27.6±0.2	-1.1±0.0	3.2±0.1	27.8±0.2

Appendix A-11 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 11 weeks.

Sample	dL*	da*	db*	dE*
PVC	-15.0±0.4	-0.3±0.1	-4.6±0.3	15.7±0.3
PVC+P/1.0	-1.8±0.2	0.1±0.1	-1.7±0.1	2.5±0.1
PVC+P/1.5	-1.5±0.1	0.1±0.0	-1.9±0.1	2.4±0.0
PVC+P/2.0	-1.7±0.2	0.2±0.0	-2.5±0.1	2.9±0.1
PVC+XT/1.0	-1.9±0.4	0.2±0.1	-1.6±0.1	2.5±0.3
PVC+XT/1.5	-1.6±0.4	0.1±0.0	-1.8±0.1	2.4±0.2
PVC+XT/2.0	-1.6±0.0	0.1±0.0	-1.5±0.1	2.2±0.1
PVC/CC	9.7±0.3	-4.3±0.0	-15.2±0.1	18.5±0.1
PVC/CC+P/1.0	9.5±0.2	-3.6±0.1	-10.0±0.3	14.2±0.3
PVC/CC+P/1.5	9.3±0.2	-3.7±0.0	-10.6±0.1	14.6±0.1
PVC/CC+P/2.0	10.1±0.6	-3.8±0.1	-10.0±0.4	14.7±0.2
PVC/CC+XT/1.0	10.7±0.6	-3.9±0.1	-9.8±0.2	15.0±0.5
PVC/CC+XT/1.5	10.1±0.6	-3.8±0.0	-9.1±0.2	14.1±0.3
PVC/CC+XT/2.0	11.2±0.7	-3.9±0.1	-8.8±0.5	14.8±0.2
PVC/TWF	31.8±0.5	-2.6±0.1	0.1±0.2	31.9±0.5
PVC/TWF+Ti1/5	14.6±0.2	-0.9±0.0	-2.1±0.0	14.8±0.2
PVC/TWF+Ti1/10	10.2±0.5	-0.7±0.0	-2.4±0.2	10.5±0.5
PVC/TWF+Ti1/15	8.4±0.4	-0.7±0.0	-2.2±0.1	8.7±0.4
PVC/TWF+Ti2/5	14.3±0.1	-0.1±0.1	1.2±0.1	14.4±0.1
PVC/TWF+Ti2/10	10.2±0.0	-0.0±0.0	0.8±0.1	10.3±0.0
PVC/TWF+Ti2/15	8.3±0.0	-0.2±0.0	0.5±0.1	8.4±0.0
PVC/TWF+P/1.0	31.4±0.3	-1.4±0.1	2.8±0.2	31.5±0.4
PVC/TWF+P/1.5	30.6±0.3	-1.3±0.0	3.6±0.0	30.8±0.3
PVC/TWF+P/2.0	30.5±0.2	-1.1±0.1	4.4±0.2	30.9±0.2
PVC/TWF+XT/1.0	31.5±0.2	-1.6±0.2	1.8±0.4	31.6±0.2
PVC/TWF+XT/1.5	30.3±0.3	-1.9±0.1	1.5±0.1	30.4±0.3
PVC/TWF+XT/2.0	30.0±0.4	-1.1±0.0	3.4±0.1	30.2±0.4

Appendix A-12 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 12 weeks.

Sample	dL*	da*	db*	dE*
PVC	-16.5±0.1	0.1±0.0	-2.5±0.1	16.7±0.1
PVC+P/1.0	-2.3±0.1	0.2±0.0	-1.5±0.1	2.7±0.1
PVC+P/1.5	-1.8±0.1	0.1±0.0	-1.8±0.1	2.5±0.0
PVC+P/2.0	-1.9±0.0	0.3±0.0	-2.4±0.0	3.1±0.0
PVC+XT/1.0	-2.0±0.0	0.1±0.0	-1.5±0.0	2.4±0.0
PVC+XT/1.5	-1.6±0.1	0.1±0.0	-1.7±0.1	2.4±0.0
PVC+XT/2.0	-1.5±0.1	-0.0±0.0	-1.5±0.0	2.2±0.0
PVC/CC	1.0±0.1	-4.3±0.1	-15.1±0.1	18.6±0.1
PVC/CC+P/1.0	9.4±0.3	-3.7±0.1	-10.4±0.1	14.5±0.2
PVC/CC+P/1.5	9.8±0.2	-3.7±0.1	-10.3±0.3	14.7±0.2
PVC/CC+P/2.0	9.9±0.2	-3.9±0.1	-10.3±0.1	14.8±0.2
PVC/CC+XT/1.0	11.1±0.2	-4.00±0.1	-9.9±0.1	15.4±0.1
PVC/CC+XT/1.5	10.7±0.3	-3.8±0.1	-8.8±0.2	14.3±0.3
PVC/CC+XT/2.0	11.2±0.8	-4.1±0.0	-9.2±0.2	15.1±0.5
PVC/TWF	32.3±0.2	-2.6±0.1	0.5±0.1	32.4±0.2
PVC/TWF+Ti1/5	14.6±0.1	-0.9±0.0	-1.9±0.1	14.8±0.1
PVC/TWF+Ti1/10	10.4±0.1	-0.8±0.0	-2.0±0.1	10.6±0.1
PVC/TWF+Ti1/15	8.1±0.1	-0.7±0.0	-1.9±0.1	8.4±0.1
PVC/TWF+Ti2/5	14.4±0.0	-0.1±0.0	1.3±0.1	14.5±0.0
PVC/TWF+Ti2/10	10.4±0.1	-0.1±0.0	0.6±0.0	10.4±0.1
PVC/TWF+Ti2/15	8.2±0.0	-0.3±0.0	0.5±0.0	8.2±0.0
PVC/TWF+P/1.0	31.4±0.2	-1.3±0.1	3.0±0.1	31.6±0.2
PVC/TWF+P/1.5	31.1±0.1	-1.1±0.0	4.1±0.0	31.4±0.1
PVC/TWF+P/2.0	30.7±0.5	-1.0±0.1	4.5±0.2	31.0±0.5
PVC/TWF+XT/1.0	31.6±0.3	-1.5±0.1	2.3±0.1	31.8±0.3
PVC/TWF+XT/1.5	30.9±0.3	-2.0±0.2	1.8±0.5	31.0±0.3
PVC/TWF+XT/2.0	30.1±0.3	-1.2±0.0	3.5±0.1	30.4±0.3

Appendix A-13 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 13 weeks.

Sample	dL*	da* db*		dE*
PVC	-16.8±0.1	0.5±0.2	-0.9±0.5	16.8±0.1
PVC+P/1.0	-2.4±0.2	0.2±0.1	-1.6±0.2	2.9±0.1
PVC+P/1.5	-2.0±0.2	0.1±0.0	-1.7±0.1	2.7±0.1
PVC+P/2.0	-2.1±0.2	0.3±0.0	-2.3±0.1	3.1±0.1
PVC+XT/1.0	-2.0±0.1	0.2±0.0	-1.5±0.1	2.5±0.1
PVC+XT/1.5	-2.0±0.3	0.2±0.1	-1.7±0.1	2.6±0.2
PVC+XT/2.0	-1.6±0.1	0.0±0.0	-1.6±0.1	2.2±0.0
PVC/CC	10.5±0.5	-4.3±0.1	-14.9±0.4	18.7±0.1
PVC/CC+P/1.0	9.0±0.2	-3.7±0.0	-11.3±0.2	14.9±0.1
PVC/CC+P/1.5	9.7±0.3	-3.6±0.1	10.9±0.4	15.0±0.1
PVC/CC+P/2.0	9.9±0.2	-3.8±0.1	-11.0±0.1	15.2±0.1
PVC/CC+XT/1.0	11.1±0.2	-4.0±0.0	-10.1±0.1	15.5±0.1
PVC/CC+XT/1.5	10.3±0.5	-3.9±0.1	-10.3±0.3	15.1±0.2
PVC/CC+XT/2.0	10.7±0.1	-4.0±0.1	-4.0±0.1 -10.0±0.3	
PVC/TWF	32.9±0.2 -2.5±0.1		1.3±0.2	33.1±0.1
PVC/TWF+Ti1/5	15.1±0.2	-0.9±0.0	-1.9±0.1	15.2±0.2
PVC/TWF+Ti1/10	10.6±0.1	-0.7±0.0	-2.1±0.0	10.8±0.1
PVC/TWF+Ti1/15	8.5±0.2	-0.7±0.0	-2.0±0.1	8.7±0.2
PVC/TWF+Ti2/5	14.9±0.3	-0.1±0.0	1.8±0.1	15.0±0.3
PVC/TWF+Ti2/10	10.6±0.1	-0.1±0.0	1.1±0.1	10.7±0.1
PVC/TWF+Ti2/15	8.3±0.1	-0.2±0.0	$0.8{\pm}0.0$	8.3±0.1
PVC/TWF+P/1.0	32.5±0.2	-1.4±0.1	2.9±0.1	32.7±0.2
PVC/TWF+P/1.5	32.3±0.2	-1.1±0.1	4.1±0.2	32.6±0.2
PVC/TWF+P/2.0	32.2±0.1	-0.9±0.1	4.7±0.2	32.5±0.1
PVC/TWF+XT/1.0	32.1±0.5	-1.5±0.1	2.3±0.4	32.2±0.5
PVC/TWF+XT/1.5	31.7±0.3	-2.0±0.0	1.7±0.0	31.8±0.3
PVC/TWF+XT/2.0	31.4±0.2	-1.2±0.1	3.6±0.0	31.6±0.2

Appendix A-14 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 14 weeks.

Sample	dL*	da*	db*	dE*
PVC	-17.0±0.2	0.6±0.2	-0.8±0.7	17.0±0.2
PVC+P/1.0	-3.0±0.1	0.2±0.1	-1.5±0.1	3.3±0.1
PVC+P/1.5	-2.2±0.1	0.1±0.1	-1.8±0.0	2.8±0.1
PVC+P/2.0	-2.6±0.3	0.3±0.0	-2.2±0.1	3.4±0.1
PVC+XT/1.0	-2.5±0.3	0.2±0.1	-1.3±0.2	2.8±0.2
PVC+XT/1.5	-2.5±0.2	0.2±0.0	-1.4±0.1	2.9±0.1
PVC+XT/2.0	-2.1±0.0	0.1±0.1	-1.3±0.0	2.1±0.1
PVC/CC	10.2±0.3	-4.5±0.1	-15.6±0.3	19.2±0.1
PVC/CC+P/1.0	10.2±0.2	-3.8±0.1	-10.6±0.1	15.2±0.2
PVC/CC+P/1.5	10.4±0.2	-3.8±0.1	-10.7±0.1	15.4±0.2
PVC/CC+P/2.0	10.4±0.5	-3.9±0.1	-10.8±0.5	15.5±0.1
PVC/CC+XT/1.0	11.1±0.1	-4.1±0.0	-10.3±0.1	15.6±0.0
PVC/CC+XT/1.5	11.3±0.5	-4.0±0.1	-10.0±0.4	15.3±0.1
PVC/CC+XT/2.0	11.5±0.2	-4.0±0.2	-9.2±0.2	15.2±0.2
PVC/TWF	34.4±0.3	-3.1±0.0	-0.1±0.0	34.5±0.3
PVC/TWF+Ti1/5	15.5±0.3	-1.2±0.0	-2.5±0.1	15.7±0.3
PVC/TWF+Ti1/10	11.0±0.3	-0.9±0.0	-2.4±0.1	11.3±0.3
PVC/TWF+Ti1/15	8.7±0.1	-0.7±0.1	-2.5±0.0	9.1±0.1
PVC/TWF+Ti2/5	15.2±0.3	-0.4±0.1	1.0±0.1	15.2±0.3
PVC/TWF+Ti2/10	10.7±0.1	-0.3±0.0	0.5±0.1	10.8±0.1
PVC/TWF+Ti2/15	8.7±0.2	-0.4±0.1	$0.4{\pm}0.0$	8.7±0.2
PVC/TWF+P/1.0	33.5±0.3	-1.7±0.0	2.5±0.1	33.6±0.3
PVC/TWF+P/1.5	33.0±0.3	-1.5±0.0	3.5±0.1	33.2±0.3
PVC/TWF+P/2.0	32.4±0.1	-1.4±0.0	3.7±0.2	32.7±0.1
PVC/TWF+XT/1.0	33.1±0.1	-2.0±0.1	1.9±0.1	33.2±0.1
PVC/TWF+XT/1.5	32.4±0.1	-2.3±0.0	1.1±0.1	32.5±0.1
PVC/TWF+XT/2.0	32.4±0.1	-1.56±0.1	2.88±0.1	32.6±0.2

Appendix A-15 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 15 weeks.

Sample	dL* da* db*		db*	dE*
PVC	-17. <mark>3±0.1</mark>	0.6±0.3	-0.9±1.1	17.3±0.1
PVC+P/1.0	-3.3±0.1	0.3±0.1	-1.4±0.0	3.6±0.1
PVC+P/1.5	-2.6±0.2	0.1±0.0	-1.7±0.1	3.1±0.1
PVC+P/2.0	-3.0±0.1	0.4±0.0	-2.9±0.1	3.7±0.1
PVC+XT/1.0	-2.7±0.1	0.2±0.0	-1.4±0.1	3.1±0.1
PVC+XT/1.5	-3.0±0.3	0.3±0.0 -1.3±0.1		3.2±0.2
PVC+XT/2.0	-2.2±0.1	0.0±0.0	-1.4±0.0	2.6±0.1
PVC/CC	10.5±0.4	-4.6±0.1	-15.7±0.2	19.4±0.1
PVC/CC+P/1.0	9.9±0.2	-3.9±0.1	-11.7±0.2	15.8±0.1
PVC/CC+P/1.5	10.0±0.3	-3.7±0.1	-11.5±0.2	15.7±0.1
PVC/CC+P/2.0	10.6±0.4	-3.9±0.0	-10.9±0.4	15.7±0.1
PVC/CC+XT/1.0	11.4±0.4	-4.1±0.0	-10.4±0.1	16.0±0.3
PVC/CC+XT/1.5	11.2±0.3	-4.1±0.0	-11.3±0.1	16.4±0.2
PVC/CC+XT/2.0	11.5±0.4	-4.1±0.1	-10.3±0.3	16.0±0.2
PVC/TWF	35.6±0.2	-3.2±0.0	0.1±0.0	35.8±0.2
PVC/TWF+Ti1/5	16.0±0.1	-1.2±0.0	-2.7±0.2	16.2±0.1
PVC/TWF+Ti1/10	11.4±0.1	-0.9±0.0	-2.9±0.1	11.8±0.2
PVC/TWF+Ti1/15	8.9±0.0	-0.7±0.1	-2.5±0.0	9.3±0.0
PVC/TWF+Ti2/5	15.6±0.1	-0.4±0.1	1.2±0.1	15.6±0.1
PVC/TWF+Ti2/10	11.2±0.2	-0.4±0.0	0.3±0.1	11.2±0.2
PVC/TWF+Ti2/15	9.2±0.1	-0.5±0.1	0.0±0.1	9.3±0.1
PVC/TWF+P/1.0	34.6±0.2	-1.8±0.1	2.8±0.2	34.7±0.2
PVC/TWF+P/1.5	34.2±0.1	-1.6±0.0	3.5±0.0	33.4±0.1
PVC/TWF+P/2.0	33.5±0.2	-1.5±0.1	3.9±0.1	33.8±0.2
PVC/TWF+XT/1.0	33.8±0.1	-2.1±0.0	1.8±0.1	33.9±0.1
PVC/TWF+XT/1.5	33.5±0.2	-2.5±0.0	1.0±0.1	33.6±0.2
PVC/TWF+XT/2.0	33.4±0.1	-1.7±0.0	2.7±0.1	33.6±0.1

Appendix A-16 The color change and the lightness change of PVC and PVC composites after exposure to sunlight for 16 weeks.

## **Appendix B**

### **Mechanical Properties of PVC and PVC Composites**

Appendix B-1 The flexural strength (MPa) of PVC and PVC composites at various exposure times for 4 months.

	Flexural strength (MPa) exposure times (months)					
Samples	0	1	2	3	4	
PVC	79.5±1.1	77.6±0.7	73.5±0.5	70.7±0.3	69.0±0.7	
PVC+P/1.0	80.9±0.9	78.0±0.9	76.7±0.5	74.8±0.4	75.3±0.4	
PVC+P/1.5	78.4±0.5	79.9±0.6	77.6±1.4	75.7±0.5	75.2±1.3	
PVC+P/2.0	79.9±0.9	78.4±1.0	76.4±0.5	75.9±0.6	75.3±1.5	
PVC+XT/1.0	79.4±0.4	77.5±0.7	7 <mark>6.4</mark> ±0.6	75.9±0.4	75.0±0.5	
PVC+XT/1.5	78.7±0.6	78.0±0.6	78.0±0.6	77.3±0.2	75.0±0.3	
PVC+XT/2.0	78.7±0.3	78.8±0.9	78.0±0.2	76.9±0.6	74.9±0.4	
PVC+CC	49.3±0.8	45.6±0.7	41.8±0.7	40.5±0.6	37.5±0.7	
PVC/CC+P/1.0	49.9±0.6	47.1±0.8	47.2±0.7	45.7±0.4	42.7±0.4	
PVC/CC+P/1.5	49.7±0.5	49.9±0.7	49.0±1.4	46.7±0.9	44.3±0.5	
PVC/CC+P/2.0	50.0±0.7	49.5±2.4	47.7±0.4	46.2±0.4	45.3±1.4	
PVC/CC+XT/1.0	48.8±0.5	47.8±0.7	48.1±0.4	45.8±0.2	42.6±0.4	
PVC/CC+XT/1.5	49.0±0.5	48.3±0.9	47.8±0.4	45.7±0.5	42.4±0.4	
PVC/CC+XT/2.0	48.9±0.7	48.7±0.5	48.8±1.2	47.2±0.5	45.1±0.3	
PVC/TWF	55.7±0.4	50.4±0.6	46.4±0.7	44.5±0.3	40.4±0.4	
PVC/TWF+P/1.0	55.0±07	56.7±1.1	53.2±0.4	49.5±0.4	46.0±0.4	
PVC/TWF+P/1.5	55.9±0.5	57.0±0.8	55.3±0.6	52.1±1.5	45.9±0.8	
PVC/TWF+P/2.0	56.0±1.3	55.6±0.8	53.4±1.3	52.2±1.5	50.0±0.9	
PVC/TWF+XT/1.0	55.2±0.4	55.4±0.9	53.2±0.7	50.5±0.5	46.1±0.2	
PVC/TWF+XT/1.5	55.7±0.5	55.8±0.7	52.8±0.4	49.7±0.6	47.5±0.3	
PVC/TWF+XT/2.0	55.5±0.3	55.9±0.7	52.1±0.3	50.7±0.6	49.4±1.0	

	Flexural modulus (GPa) exposure times (months)					
Samples	0	1	2	3	4	
PVC	2.9±0.1	3.0±0.0	2.8±0.1	2.5±0.0	2.4±0.1	
PVC+P/1.0	2.9±0.1	3.0±0.1	2.9±0.2	2.8±0.0	2.7±0.1	
PVC+P/1.5	2.8±0.1	3.0±0.1	2.7±0.0	2.8±0.1	2.6±0.1	
PVC+P/2.0	2.9±0.2	3.0±0.1	2.7±0.2	2.7±0.1	2.8±0.2	
PVC+XT/1.0	3.0±0.0	3.0±0.0	2.8±0.1	2.8±0.1	2.8±0.1	
PVC+XT/1.5	3.0±0.1	3.2±0.1	3.0±0.1	3.0±0.0	2.6±0.2	
PVC+XT/2.0	2.9±0.1	2.9±0.0	3.1±0.0	3.1±0.1	2.8±0.1	
PVC+CC	3.6±0.3	3.2±0.2	2.8±0.1	2.2±0.1	2.2±0.1	
PVC/CC+P/1.0	3.6±0.2	3.1±0.1	2.9±0.0	2.7±0.2	2.5±0.1	
PVC/CC+P/1.5	3.7±0.1	3.2±0.1	2.8±0.1	2.7±0.1	2.5±0.1	
PVC/CC+P/2.0	3.4±0.2	3.3±0.1	3.0±0.1	3.0±0.2	2.5±0.1	
PVC/CC+XT/1.0	3.9±0.4	3.3±0.1	2.9±0.1	2.7±0.1	2.5±0.1	
PVC/CC+XT/1.5	3.5±0.2	3.5±0.2	3.3±0.4	2.8±0.1	2.6±0.1	
PVC/CC+XT/2.0	3.8±0.2	3.2±0.1	2.9±0.1	3.2±0.1	2.6±0.1	
PVC/TWF	4.9±0.5	4.0±0.2	4.0±0.3	3.8±0.2	3.0±0.1	
PVC/TWF+P/1.0	5.6±0.2	4.9±0.3	3.8±0.2	4.0±0.4	3.6±0.1	
PVC/TWF+P/1.5	5.6±0.1	4.9±0.2	4.3±0.3	5.1±0.4	3.6±0.2	
PVC/TWF+P/2.0	5.2±0.2	4.6±0.3	5.0±0.2	4.9±0.2	4.3±0.1	
PVC/TWF+XT/1.0	5.7±0.6	5.3±0.6	4.9±0.1	4.2±0.1	3.3±0.2	
PVC/TWF+XT/1.5	5.3±0.3	5.0±0.3	4.6±0.2	4.2±0.2	4.5±0.2	
PVC/TWF+XT/2.0	5.1±0.1	4.9±0.3	3.8±0.2	3.8±0.1	4.3±0.2	

**Appendix B-2** The flexural modulus (GPa) of PVC and PVC composites at various exposure times for 4 months.

	Ten	(IPa) exposure	are times (months)		
Samples	0	1	2	3	4
PVC	54.3±0.3	55.1±0.4	53.0±0.4	49.2±0.3	48.2±1.3
PVC+P/1.0	53.9±0.7	53.4±0.8	52.5±0.4	51.4±0.4	51.0±0.4
PVC+P/1.5	54.4±0.6	55.4±1.4	54.2±1.3	52.9±0.5	51.8±0.6
PVC+P/2.0	54.6±0.3	56.8±1.3	54.4±0.4	53.2±0.5	52.3±1.5
PVC+XT/1.0	53.7±0.9	53.2±0.6	53.0±0.6	53.2±0.7	51.5±0.9
PVC+XT/1.5	54.1±0.7	54.4±0.2	55.5±0.4	54.3±0.4	50.8±0.3
PVC+XT/2.0	54.7±0.4	54.5±0.3	55.4±0.6	54.3±0.7	52.8±0.7
PVC+CC	33.7±0.4	31.3±0.4	28.4±0.2	25.9±0.5	23.9±0.5
PVC/CC+P/1.0	34.7±0.4	33.3±0.5	33.2±1.1	31.8±0.6	26.6±0.4
PVC/CC+P/1.5	34.5±0.4	33.8±0.8	32.4±0.6	31.9±0.5	29.1±0.5
PVC/CC+P/2.0	33.3±0.9	34.1±0.3	33.1±0.9	32.3±0.7	29.8±0.5
PVC/CC+XT/1.0	33.4±0.3	31.5±0.6	31.4±0.3	30.6±0.4	26.8±0.4
PVC/CC+XT/1.5	33.2±0.7	32.0±0.7	31.7±0.7	30.3±0.4	26.9±0.7
PVC/CC+XT/2.0	34.1±0.7	33.2±1.0	32.5±0.5	31.2±0.4	28.8±1.3
PVC/TWF	40.0±0.6	36.3±0.4	32.3±0.6	30.0±0.8	26.2±0.5
PVC/TWF+P/1.0	40.5±0.4	40.6±0.6	38.7±0.3	36.7±0.3	34.8±0.6
PVC/TWF+P/1.5	39.4±1.6	40.2±0.6	37.4±1.4	36.0±0.4	34.3±0.7
PVC/TWF+P/2.0	37.7±0.4	38.5±0.4	36.6±0.2	34.8±0.5	32.9±0.6
PVC/TWF+XT/1.0	38.1±0.4	38.0±0.5	37.1±0.4	35.8±0.5	32.2±0.8
PVC/TWF+XT/1.5	38.6±0.5	38.2±0.9	38.0±0.3	35.2±0.5	31.6±0.7
PVC/TWF+XT/2.0	37.9±0.7	36.3±0.5	37.7±0.3	34.7±0.5	33.2±0.8

**Appendix B-3** The tensile strength (MPa) of PVC and PVC composites at various exposure times for 4 months.

	Tensile modulus (GPa) exposure times (months)					
Samples	0	1	2	3	4	
PVC	2.5±0.1	2.6±0.0	2.5±0.1	2.4±0.0	2.2±0.1	
PVC+P/1.0	2.8±0.3	2.6±0.2	2.6±0.2	2.5±0.0	2.4±0.0	
PVC+P/1.5	2.6±0.1	2.6±0.1	2.5±0.1	2.6±0.1	2.4±0.0	
PVC+P/2.0	2.5±0.0	2.5±0.0	2.4±0.0	2.4±0.0	2.4±0.0	
PVC+XT/1.0	2.4±0.0	2.4±0.0	2.3±0.1	2.5±0.0	2.5±0.1	
PVC+XT/1.5	2.6±0.1	2.5±0.0	2.5±0.0	2.5±0.1	2.4±0.1	
PVC+XT/2.0	2.4±0.0	2.5±0.1	2.5±0.0	2.6±0.0	2.5±0.1	
PVC+CC	3.4±0.1	3.0±0.2	2.7±0.1	2.4±0.1	2.2±0.0	
PVC/CC+P/1.0	3.3±0.0	3.3±0.1	2.9±0.1	3.0±0.1	2.3±0.1	
PVC/CC+P/1.5	3.3±0.1	3.2±0.1	2.9±0.1	2.8±0.1	2.6±0.0	
PVC/CC+P/2.0	3.3±0.1	3.1±0.1	2.9±0.1	2.9±0.1	2.5±0.1	
PVC/CC+XT/1.0	3.0±0.0	3.0±0.1	2.6±0.1	2.8±0.0	2.3±0.0	
PVC/CC+XT/1.5	3.1±0.2	2.9±0.1	2.6±0.1	2.7±0.1	2.3±0.1	
PVC/CC+XT/2.0	3.0±0.1	3.0±0.1	2.8±0.1	2.9±0.1	2.6±0.1	
PVC/TWF	4.0±0.2	3.7±0.1	3.7±0.1	3.0±0.1	2.6±0.0	
PVC/TWF+P/1.0	4.5±0.4	4.2±0.2	3.8±0.1	3.8±0.2	3.5±0.0	
PVC/TWF+P/1.5	4.2±0.2	4.0±0.1	3.8±0.1	3.7±0.1	3.6±0.1	
PVC/TWF+P/2.0	4.4±0.4	3.9±0.2	3.5±0.1	3.5±0.1	3.6±0.1	
PVC/TWF+XT/1.0	4.3±0.1	4.0±0.1	3.6±0.1	3.7±0.3	3.8±0.1	
PVC/TWF+XT/1.5	4.3±0.1	3.9±0.1	3.9±0.1	3.8±0.1	3.3±0.1	
PVC/TWF+XT/2.0	4.3±0.1	3.6±0.1	3.9±0.3	3.8±0.0	3.4±0.2	

**Appendix B-4** The tensile modulus (GPa) of PVC and PVC composites at various exposure times for 4 months.

### VITA

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