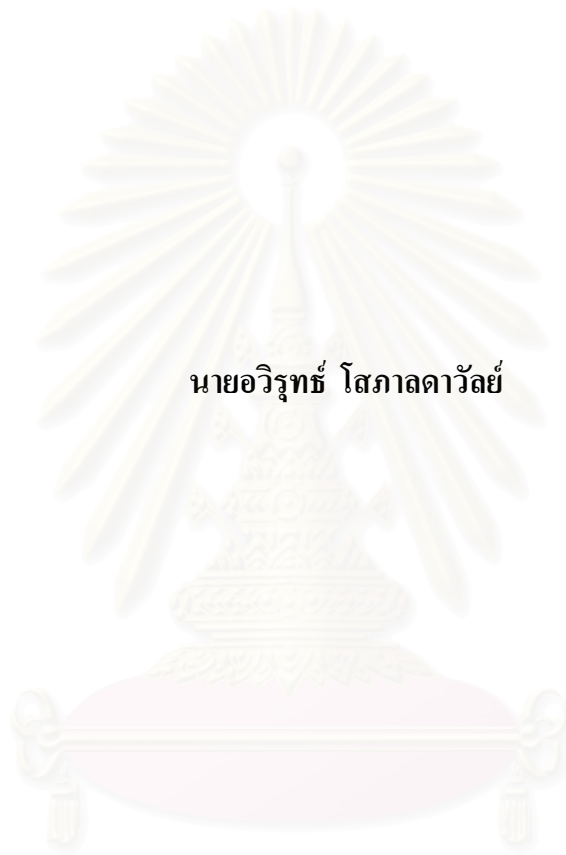


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**DEGRADATION OF PHOTSENSITIZED CALCIUM
CARBONATE FILLED HDPE FILM**



Mr. Awirut Sopaladawan

**สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย**
**A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science**

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CARBONATE FILLED HDPE FILM**

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อวิรุทธ์ โสภาลดาวัลย์ : การสลายตัวของฟิล์มเอชดีพีอีไวแสงเติมด้วยแคลเซียมคาร์บอเนต (DEGRADATION OF PHOTSENSITIZED CALCIUM CARBONATE FILLED HDPE FILM) อ.ที่ปรึกษา : ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ อ.ที่ปรึกษาร่วม : รศ.ดร.ศุภวรรณ ดันตยานนท์, 74 หน้า. ISBN 974-17-1068-2

ฟิล์มเอชดีพีอีและฟิล์มเอชดีพีอีเติมด้วยแคลเซียมคาร์บอเนตถูกเร่งด้วยสารไวแสงจำพวกอะโรมาติกคีโตน และอะโรมาติกไดคีโตน ถูกนำไปทดสอบกลางแจ้งเป็นเวลา 12 สัปดาห์เพื่อศึกษาผลของแคลเซียมคาร์บอเนต และสารไวแสง และความก้าวหน้าของการสลายตัว โดยวัดการเปลี่ยนแปลงค่าความต้านทานแรงดึง ค่าการยืดเมื่อขาด น้ำหนักโมเลกุลเฉลี่ย และค่าการดูดกลืนรังสีอินฟราเรด หลังการทดสอบกลางแจ้งการดูดกลืนรังสีอินฟราเรดสัมพันธ์ของหมู่คาร์บอนิลเพิ่มขึ้น ส่วนค่าความต้านทานแรงดึง ค่าการยืดเมื่อขาด และน้ำหนักโมเลกุลเฉลี่ย ลดลงตามการเพิ่มขึ้นของเวลา

จากผลการทดลองพบว่า ฟิล์มเอชดีพีอีไม่มีการเปลี่ยนแปลงที่มีนัยสำคัญระหว่างการทดสอบกลางแจ้ง สำหรับฟิล์มผสมแคลเซียมคาร์บอเนตในปริมาณมากมีอัตราการสลายตัวสูงขณะที่มีค่าความต้านทานแรงดึงและค่าการยืดเมื่อขาดน้อยมากหลังการทดสอบกลางแจ้ง 12 สัปดาห์ แคลเซียมคาร์บอเนตที่ผสมในฟิล์มเอชดีพีอีไม่ก่อให้เกิดสารประกอบคาร์บอนิล แต่การเติมสารไวแสงจะช่วยเสริมให้เกิดสารประกอบคาร์บอนิลเพิ่มขึ้น อย่างไรก็ตามฟิล์มที่ผสมสารไวแสงมีการสูญเสียสมบัติมากกว่าฟิล์มที่ไม่ผสมสารไวแสง เมื่อพิจารณาชนิดของสารไวแสงฟิล์มที่ผสมสารไวแสง 2-เมทิลแอนทราควิโนน แสดงอัตราการสลายตัวสูงกว่า ฟิล์มที่ผสมสารไวแสงเบนโซฟีโนน

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา	ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต.....
หลักสูตร	ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่ออาจารย์ที่ปรึกษา.....
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CALCIUM CARBONATE FILLED HDPE FILM. THESIS ADVISOR :
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HDPE and calcium carbonate filled HDPE films sensitized with aromatic ketone and aromatic diketone were exposed outdoor for 12 weeks. The effect of calcium carbonate filler and photosensitizers and the progress of degradation were studied by measuring the changes in tensile strength, elongation at break, average molecular weight and fourier transform infrared absorption. The relative infrared absorbances of the carbonyl group increased after exposure. The tensile strength, elongation at break and average molecular weight decreased with increasing exposure time.

According to the results, it was found that the HDPE film did not change significantly during the outdoor exposure. For the HDPE films filled with high contents of calcium carbonate, the degradation rate was high whereas tensile strength and elongation at break were very low after 12 weeks of exposure. Calcium carbonate content in HDPE films did not generate carbonyl group but the photosensitizer could. However, the samples containing the photosensitizers, lose their properties more than the ones without photosensitizers. Regarding the type of photosensitizers, samples sensitized with 2-methylantraquinone show a higher degradation rate than the ones sensitized with benzophenone.

Field of study Petrochemistry and Polymer Science Student's signature.....

Program Petrochemistry and Polymer Science Advisor's signature.....

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CHAPTER I

INTRODUCTION

1.1 The Purpose of the Investigation

During recent decades, there has been a continuous increase in the use of commodity plastics for packaging application and this has led to an increase in the amount of plastic waste. The high-density polyethylene waste has affected the overall composition of municipal solid waste and caused an undesirable increase in the volume/weight ratio of garbage. Furthermore, the plastic waste may represent an undesirable pollutant in many ecosystems (i.e. to soil, freshwater and marine habitats) because they are generally inherently inert to attack by microorganism or by chemicals in the environment.

To overcome these problems, the degradable plastics must be developed. The most frequently used approach is an introduction of sensitizer into polymer, the excited compound either decomposes into free radicals and initiates degradation or oxidation of the polymer as well as the blends of plastics with filler but the blends macroradicals are generated and can be terminated by oxygen in the air, leading to the introduction of polar group onto polymer chains.

Filler with hydrophilicity or polarity and polymer with polar groups could facilitate interfacial bonding. Therefore, whether or not polymer molecules bear polarity is an important factor determining the reinforcement effect in plastic composite. In order to achieve good interfacial adhesion between polymer and filler, it is necessary for this kind of plastic to bear polar groups before a good affinity with fillers can be brought about.

Calcium carbonate filled polymer for a variety of purposes for example to enhance mechanical properties and dimensional stability, to control opacity and improve surface printability. Calcium carbonate, due to its low cost, is one of the more favorable additives.

1.2 Objectives

The objectives of this research are as follows:

1. To prepare the calcium carbonate filled high-density polyethylene films and photosensitized calcium carbonate filled high-density polyethylene films.
2. To study the properties of the calcium carbonate filled high-density polyethylene films and photosensitized calcium carbonate filled high-density polyethylene films.
3. To investigate the effect of outdoor exposure on the change of mechanical properties, the molecular weights and absorbance properties with fourier-transform infrared absorption.

1.3 Scope of the Investigation

For the preparation of high-density polyethylene films with and without filler and additives, the appropriate compositions were studied. The suitable filler and additives content in high-density polyethylene films yielded the good mechanical properties and the degradation rate was determined. The necessary procedures to carry out the work are as follows:

1. Literature survey and in-depth study of this research work.
2. Preparation of the calcium carbonate filled high-density polyethylene films and photosensitized calcium carbonate filled high-density polyethylene films by blowing film machine.
3. Study of the properties of the calcium carbonate filled high-density polyethylene films and photosensitized calcium carbonate filled high-density polyethylene films.
4. Study of the effect of outdoor exposure test for 12 weeks.
5. Investigation of the properties of films such as tensile strength, elongation at break, molecular weight and carbonyl index.
6. Summarization of the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 High-Density Polyethylene [1]

By historical definition, high density polyethylene, HDPE is the product of ethylene polymerization with density 0.94 g/cm^3 and above. Its structure is linear because of the absence of branches or contains a small number of chain branches and is a non-polar, hydrophobic polymer

At present, two classes of catalysts are used for the commercial manufacturer of HDPE: those based on chromium oxide, e.g., Phillips catalyst, and those based on Ziegler-Natta systems. Other catalysts based on other transition metals are known, including scandium, titanium, chromium, cobalt, nickel, molybdenum and rhodium, although these have not achieved commercial significance.

The technologies available for HDPE manufacture are solution, slurry or suspension, and gas-phase polymerization. Solution polymerization is the oldest and most widely used method because of easy and flexibility and this technology is the only one capable of producing the full range of HDPE grades, from low molecular weight waxes to ultra high molecular weight HDPE. Gas- phase polymerization, the newest technology, is increasingly utilized because of the low investments and operating costs.

Because of the high crystallinity of HDPE, thin HDPE film is translucent and low transparency. In general, it exhibits low chemical reactivity and is not soluble in any solvent at room temperature. Due to its inertness and absence of toxicity, HDPE is employed on a large scale in food and blown-film products.

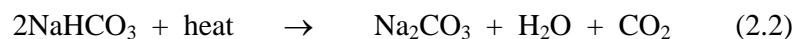
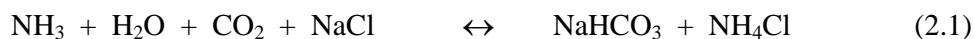
2.2 Calcium Carbonate [2, 3]

CaCO_3 is one of the earth's most abundant minerals, found in various forms all over the world. It is a very stable mineral, forming entire mountain ranges in addition to portions of seashores composed of coral and mollusk shell. In living organisms from simple seashells, coral, and mollusks to the most highly advanced vertebrate-structures containing CaCO_3 provide protection and support. Skeletal structures containing calcium phosphate and CaCO_3 far outlast all other body parts.

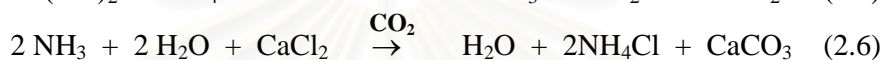
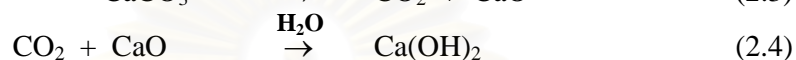
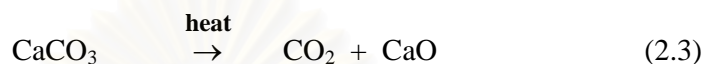
Owing to the varied geologic history of CaCO_3 deposits, many different forms are recognized, such as limestone, marble, calcite, chalk, aragonite and dolomite (calcium-magnesium carbonate). Among these, calcite and chalk, as well as man-made precipitated grades, are the most commercially developed forms.

Calcium carbonate is the most widely used filler or extender pigment in the plastics industry. Polyolefins, poly(vinyl chloride), polyesters, phenolics and epoxies are all resins with which calcium carbonate can be compounded. This broad usage can be attributed to both economic and performance considerations. Current commercial grades include finenesses not available a decade ago, as well as surface-modified grades to promote ease of wetting and dispersion, which permit higher loadings.

Ernest Solvay, a Belgian, in 1864, successfully manufactured Na_2CO_3 by an ammonia process in Equations. 2.1-2.6. Naturally occurring CaCO_3 is starting material and in this process precipitated CaCO_3 is a by-product. Production of the by-product is limited by amount of main product produced. Precipitated CaCO_3 is washed to remove soluble salts, then dried and micropulverized. The particle size is controlled by conditions of precipitation: temperature, concentration, rate and order of addition of ingredients, and amount of agitation. Particle sizes are fairly uniform and can be varied from about 0.03-0.05 micrometre up to about 8-10 micrometre. Impurities are NaCl and water. Precipitated CaCO_3 is used in specialized applications where purity, fineness, uniform particle size, and excellent whiteness justify their higher cost.



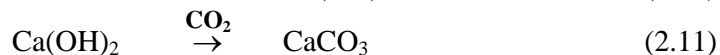
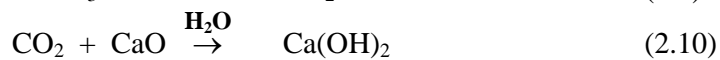
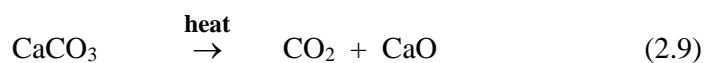
CaCO₃ is used in this process as follows:



Since 1940, more NaOH has been produced electrolytically than by the “lime-soda” process. Therefore, the production of precipitated CaCO₃ by this process is necessarily limited. CaCO₃ is heated to form CaO and reacted with water to form calcium hydroxide (Ca(OH)₂). The Ca(OH)₂ is then reacted with sodium carbonate to form calcium carbonate and sodium hydroxide. The CaCO₃ settles out, is removed and washed to remove NaOH. In Equations 2.7 and 2.8, fine particle size CaCO₃ is produced by this method.



Since Solvay process and soda-lime plants are being closed for economic reasons, less by-product CaCO₃ is available. However precipitated CaCO₃ is still required, it is manufactured by recarbonation in Equations 2.9-2.11. The product is aragonite, with higher specific gravity than calcite. Median particle sizes are between 0.2 and 2.0 micrometre and particle size distribution is wider than the previous two precipitated materials.



Purified fine ground CaCO_3 has the widest usage in plastics because it is purified by chemical and/or physical removal of iron and silica to minimize the degradation of plastics, and is ground fine enough to provide good physical properties in highly filled plastic compounds. The stone is usually quarried, but in some cases underground mining is used. The crude rock is “crushed” in a jaw or roll crusher to pass through a 3-inch screen, and further particle size reduction can occur in pot crushers, rotary hammer mills, or similar mills to reach 100 mesh in size.

Chemical floatation or mineral dressing to remove impurities can be done at this size reduction process. Particle size reduction can continue using dry or water grinding techniques, utilizing grinding media. Once the general particle size range is reached, classification techniques may function to produce select particle size distributions. Water-ground products are shipped as slurry or dried and micronized. This type of process will generally be used for products having a median particle diameter of 0.6-10 micrometre.

Coated CaCO_3 is currently available in several finenesses, both natural ground and precipitated, and almost all the commercially available products are coated with stearic acid or calcium stearate. In many resins the coating leads to improved filler dispersion and superior rheological and physical properties. While most manufacturers consider their coating procedures proprietary, stearic acid-coated CaCO_3 can easily be produced in laboratory batches by the use of a high intensity mixer. The CaCO_3 is heated to a temperature above the melting point of the stearic acid, at which point the acid is introduced into the mixer. Coating levels are nearly always directly related to filler surface area.

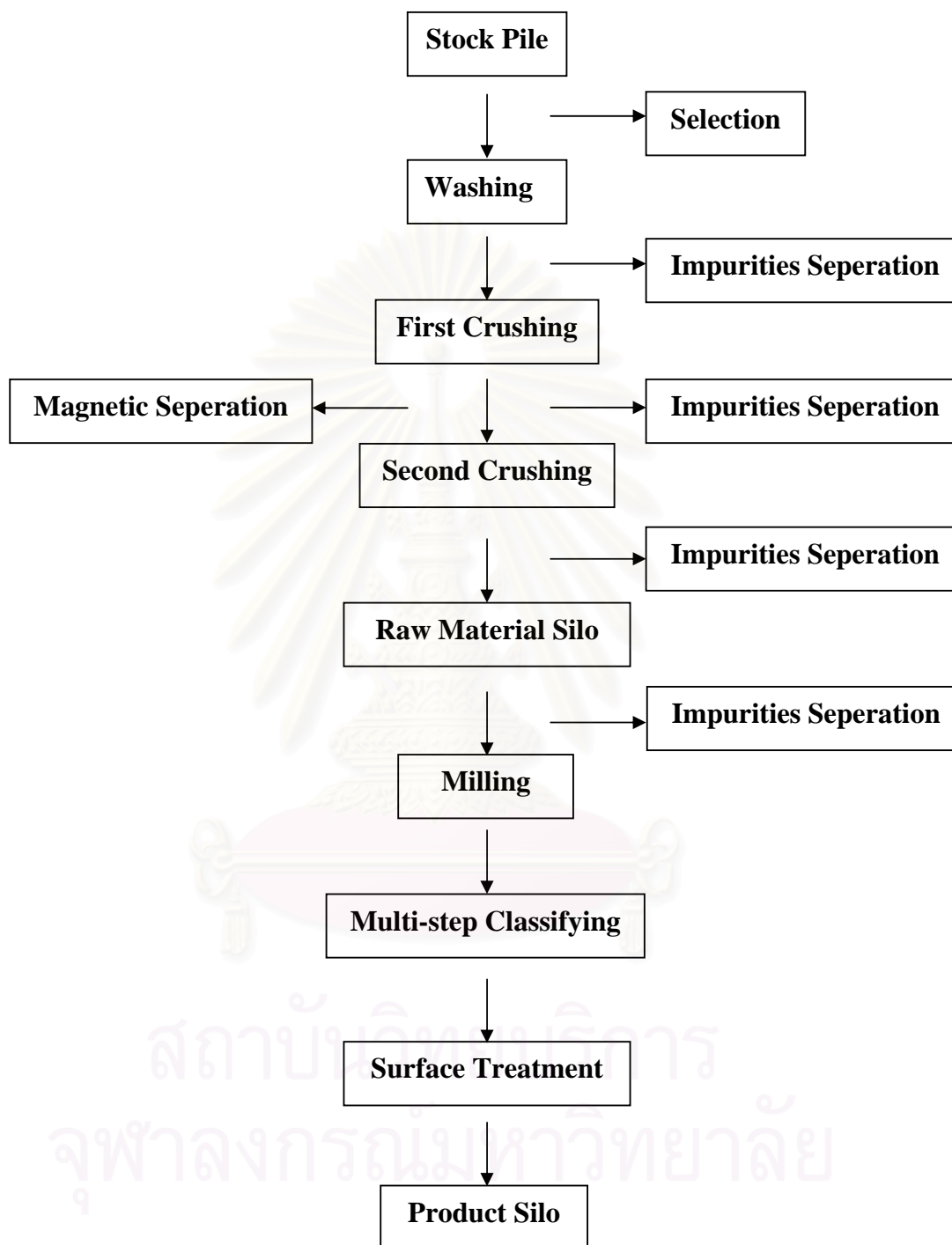


Figure 2.1 Purified fine ground CaCO_3 process

2.3 Calcium Carbonate Filled High Density Polyethylene Film [4, 5, 6]

Particulate-filled polymers have become an increasingly important industrial technique. It is an economically viable and versatile way in which new materials can be prepared to have a wide range of properties.

High density polyethylene (HDPE) has been filled with mineral particles for variety of purposes, for example to enhance mechanical properties and dimensional stability, to control opacity and barrier properties. CaCO_3 , because of its low cost, is one of the more favorable additives. However, the higher polar nature and higher surface areas of CaCO_3 particle cause difficulties in dispersion and stability. High density polyethylene readily accept CaCO_3 at loading 20-50% by weight. Poor dispersion leads to production of non-homogeneous final products and reduces physical properties. Considerable effort has been devoted to finding ways to increase the physical properties of loaded high density polyethylene, such as copolymerizing polar groups in the polymer chain, or crosslinking the filled polyethylene with an organic peroxide. Recent work indicates that the use of coated CaCO_3 or addition of coupling agent will lead to better properties. The most common compatibilized way is the introduction of a third component, usually one functional polymer, to the blends which promotes interfacial interaction between matrix and dispersed phase.

Functional polymers, used as compatibilizer, are macromolecules to which chemically functional groups are attached. In common, a required active functional group can be introduced onto a polymer chain. Recently, a new method to functionalize polyolefin has been developed through filling process (Mechanochemical modification) such as CaCO_3 filled HDPE resin can be successfully achieved good interfacial adhesion, it is necessary for this kind of plastics to bear polar groups before a good affinity with fillers can be brought about. In this case chemical bonds in HDPE chains can be ruptured during processing in extruders by stress-induced reaction, a field commonly called mechanochemistry. Macroradicals are generated and can be terminated by oxygen in the air, leading to the introduction of polar groups onto HDPE chain as shown in Equations 2.12-2.15 and Figures 2.2. CaCO_3 has found wide application as a polymer filler owing to a useful combination of properties.

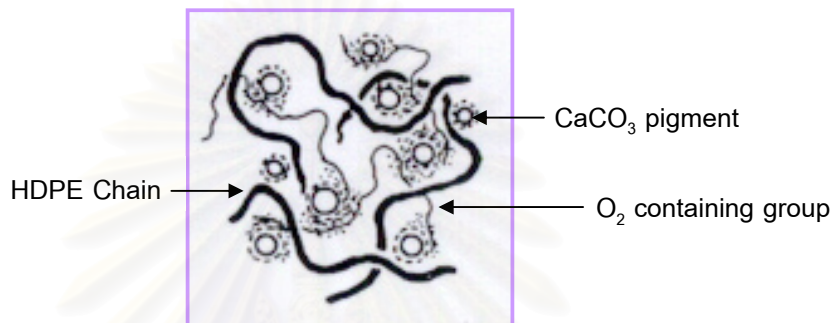
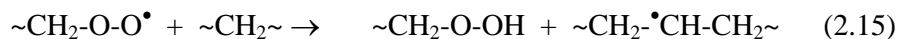
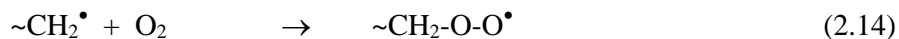
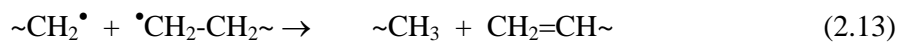
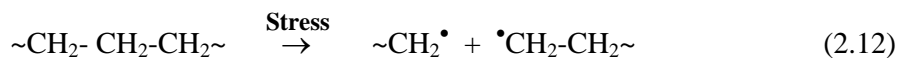
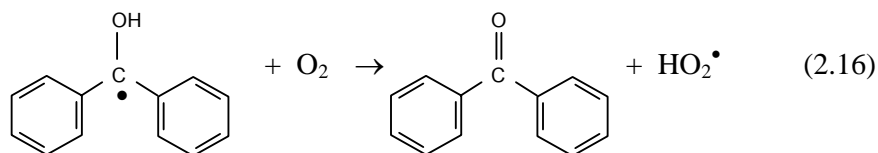


Figure 2.2 Schematic representation for interfacial filling process [7]

2.4 Sensitized Photo-Degradation [8, 9]

A photosensitizer usually has a high absorption coefficient for ultraviolet light; the excited compound either decomposes into free radicals and initiates degradation or oxidation of the polymer, or it transfers the excitation energy to the polymer (or to oxygen). A good sensitizer should be easily admixed with the polymer and must not decompose thermally or in the dark.

Aromatic ketones and diketones abstract hydrogen or decompose after excitation and cause the initiation of photochemical processes, for example, excited benzophenone can abstract hydrogen from the polymer, or the radical formed from benzophenone can react with oxygen and form a hydroperoxide radical and regenerate a benzophenone molecule:

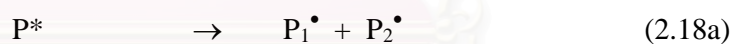


Quinones behave similarly: their excited state has biradical character, the biradical abstracts hydrogen from the polymer and hydroquinone forms, for example, the addition of various quinones sensitizes the photodegradation of polyisoprene solutions. The sensitizing effect is drastic, especially with anthraquinone.

Ketone and quinone such as benzophenone and 2-methylantraquinone have been frequently used in order to initiate or accelerate photo-degradation. These compounds are capable of effectively absorbing ultraviolet light at $\lambda > 300$ nm and decomposes into free radicals and initiates degradation or oxidation of the polymer, or it transfers the excitation energy to the polymer.

Sensitization process leads to the rapid photo-degradation of the polymer to low molecular weight compounds that are small enough to be decomposed by microorganism.

Recently the term sensitization has been used by photochemistry to solely denote processes involving energy transfer that is subsequently followed by a chemical reaction or physical process, such as luminescence as shown in Equations 2.17 and 2.18.



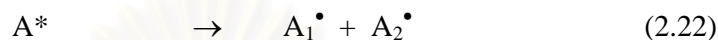
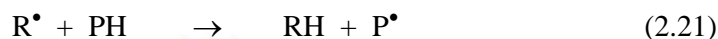
In conjunction with sensitization, it is appropriate to discuss also processes such as hydrogen abstraction, that are initiated by electronically excited additives according to Equation 2.19.



Sometimes excited initiator molecules react primarily with a low molecular weight compound (Eq. 2.20).



The free radicals produced in reaction (2.20) might subsequently attack the polymer (Equation 2.21) and processes originated by excited initiator molecules dissociating readily into free radicals after excitation (Equation 2.22).



where A	=	Additive
A*	=	Additive electrically excited state
P	=	Polymer
P*	=	Polymer electrically excited state
PH	=	Macromolecule
RH	=	Low molecular weight molecule
P [•]	=	Macroradical
R [•]	=	Free radical

2.5 Photo-Oxidation of Polyethylene [10, 11]

Photo-oxidation is caused mainly by the presence of catalyst residues, hydroperoxide groups, carbonyl groups and double bonds. This covers degradation reactions carried out in the presence of oxygen and is very closely related to outdoor exposure.

Outdoor exposure was soon recognized as an important factor in the deteriorative aging and weathering processes which occur in commercial polymer. The reasons for this are readily understood. The wavelength of the radiation from the sun which reaches the earth's surface extends from the infrared (>700 nm), through the visible spectrum (approximately 400-700 nm) into the ultraviolet (<400 nm) with a cutoff at approximately 300 nm depending upon atmospheric conditions. The energies of 700-400 and 300 nm photons are approximately 170, 300 and 390 kJ mol⁻¹ respectively. The strengths of C-C and C-H bonds are approximately 420 and 340 kJ mol⁻¹ respectively although they may be very much less in certain environments, for example in the neighbourhood of aromatic or unsaturated structures. Thus, it is clear

that the energy of the quanta of the ultraviolet and possibly of the visible components of sunlight is sufficient to break chemical bonds and that the shorter wavelengths will be the more effective.

Of course, it is not enough that sufficiently energetic quanta are available. Chromophoric groups are necessary to absorb the incident radiation. In polymers, these are usually unsaturated structures such as carbonyl, ethylenic or aromatic group. Various chromophores originally present in the polymer, accumulated during processing and storage, or added intentionally to the polymer may have an important effect on photostability.

Absorption of radiation is an essential first step to photo-degradation, strongly absorbed radiation will be attenuated as it passes through the polymer and reaction will be concentrated in the surface layers. It is for this reason that a "skin effect" is frequently observed in photo-initiated reactions.

The first chemical step in photo-degradation is usually homolytic bond scission to form free radical. These radicals will normally react rapidly with any oxygen present. In this way, visible and especially ultraviolet radiation are particularly effective initiators of oxidation.

In the photo-oxidation the sample thickness is even more important than in thermal degradation. The extent of oxidation mainly occurs in a very thin surface layer of the material. The molecular weight of the polyolefins rapidly decreases during photo-oxidation.

The outdoor exposure of polyethylene causes the formation of various free radicals. Some of these radicals combine with oxygen dissolved in the polymers to initiate chain reaction and form thermally unstable products. The oxidative process will involve peroxy radicals attack on the polymer. Hydroperoxide (ROOH) are believed to slowly breakdown and produce carbonyl compounds. The carbonyl compounds are predominant those expected from the Norrish type I and II process. Carbonyl groups may also participate in the photo-oxidation of polymers by a less direct route. The photo-excited triplet carbonyl groups may be quenched by ground state molecular oxygen to form excited singlet oxygen ($^1\text{O}_2$). The singlet oxygen may then react with any unsaturation in the polymer such as vinyl groups produced in the Norrish II process to form hydroperoxides as shown in Figure 2.7.

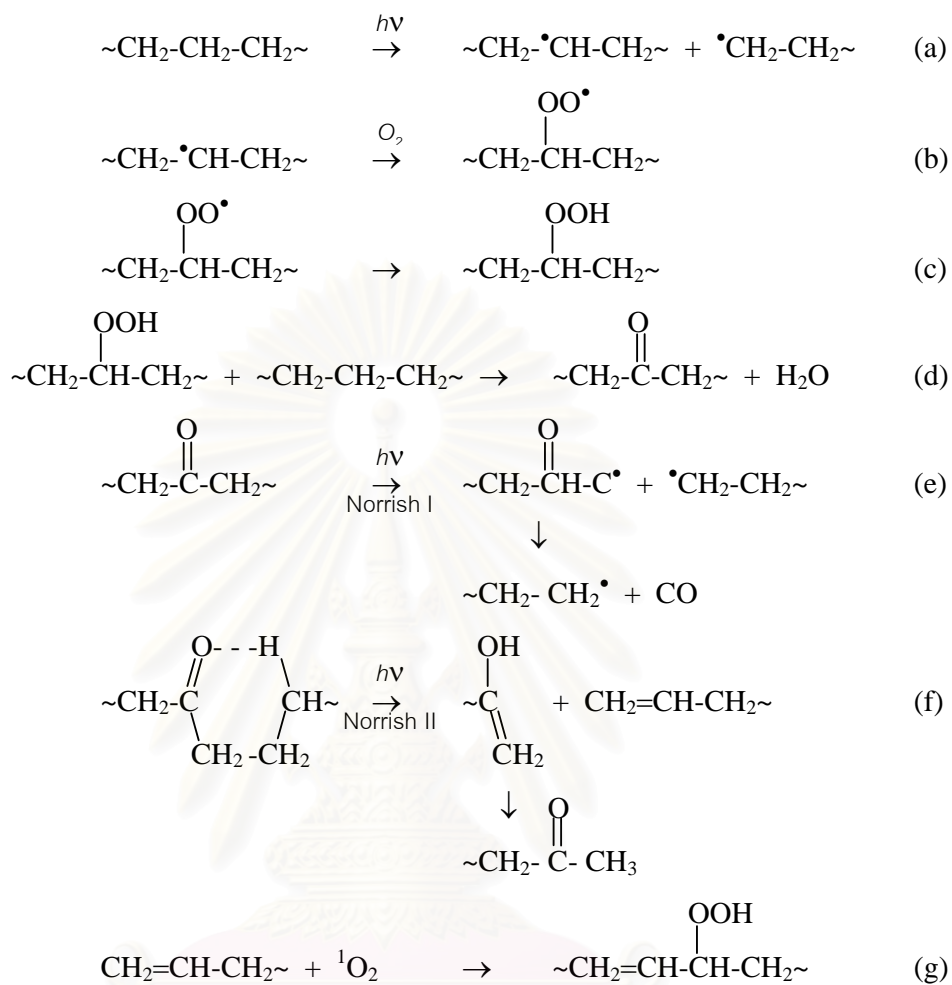


Figure 2.3 Photo-oxidation reaction of polyethylene [8]

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2.6 Literature Review

Many investigators studied the degradation of plastics in different ways. The works reported on the changes of artificial weathering and natural weathering with and without introducing additives and/or filler into plastics. The physical properties and characters of degradable plastics were observed. Some works were summarized as follows:

Wang, Q., Chen, H. and Liu, Y. [12] studied the compatibilizing effect of the grafting of maleic anhydride (MAH) onto low-density polyethylene (LDPE) prepared by pan mill mechanochemical reactor on calcium carbonate filled HDPE. The pulverization and stress degradation of LDPE in mechanochemical process was investigated. It was found that LDPE-g-MAH could improve the compatibility between polymer matrix and inorganic fillers obviously, and enhance the mechanical properties of the composites to a great degree.

Huang, H. [13] studied the effect of stress induced reaction on the crushing and structure of HDPE matrix and the properties of CaCO_3 filled HDPE. The change in morphology, structure, dynamic mechanical properties, rheological properties and mechanical properties of blends before and after pan milling were investigated. In the presence of calcium carbonate, milling efficiency was improved, and time needed for each cycle was greatly decreased. Oxygen-containing polar groups that were introduced onto HDPE chains through mechanochemical reaction during milling enhanced interfacial adhesion between HDPE and polar CaCO_3 and thus improved the dispersion and distribution of CaCO_3 particles in the blends. Rheological, thermal and mechanical properties were also improved.

Lei, J. [14] studied the effect of compatibilizer, HDPE functionalized by ultraviolet irradiation (uHDPE) on CaCO₃ filled HDPE. Mechanical properties and interfacial interactions between CaCO₃ and the polymers were evaluated by SEM, ESCA and solvent extraction. It was found that ultraviolet irradiation in air introduces the following oxygen containing group on HDPE chain and the concentration of these groups increases with irradiation time. The addition of a small amount (<10% by weight) of uHDPE chain to CaCO₃ filled HDPE improves the tensile and impact strength. The morphology of the compatibilized compound is nearly homogeneous and no CaCO₃ sediment was observed in a hot xylene solution of HDPE/uHDPE/CaCO₃ when the content of uHDPE exceeded 30% by weight.

Satoto, R., et al. [15] studied weathering test of high density polyethylene at different latitudes. It was found that the chemical change in terms of carbonyl absorbance and the enthalpies of melting are increased slightly, suggesting that natural weathering of HDPE occurred at two different latitudes. The samples exposed in Bundung (17°NL, 108°EL) as representative of a tropical zone showed a constant group growth throughout the year, while in Tsukuba (35°NL, 140°EL) as a temperate zone, carbonyl group growth varied during the year. Thus, temperature is more important factor than solar radiation. During the initial stage of exposure, the shape and the size of melting peaks are similar and the enthalpies of melting are increased slightly, suggesting that crystallinity increased.

Andrady, A.L. [16] studied the outdoor weathering of polyethylene homopolymer under exposure in air and in sea water. Photo-oxidative degradation of polyethylene films as monitored by changes in the tensile properties, particularly the mean ultimate extension, was markedly lower when the samples were exposed outdoors, floating on sea water, compared to those exposed in air. The slower rates of degradation in sea water were possibly due to the samples being maintained at a relatively lower and stable temperature in sea water compared to those exposed in air. A similar study on a commercially available enhanced photo-degradable PE was found to undergo rapid loss in ultimate tensile extension, even where the samples

were exposed floating in sea water. The rate of degradation was marginally slower in sea water than in air, but the samples were embrittled in both cases.

Tanaka, A., et al. [17] studied morphology of low density polyethylene films on photo-degradation by weather meter. Films with different degrees of crystallinity and different degrees of orientation were prepared and subjected to photo-degradation at 336 K for 12 days. The rheological and GPC measurement was made. It was found that the induction period and the rate of degradation hardly change with heat treatment condition, that is, the degree of crystallinity. The rheological and GPC measurements indicated that photo-degradation causes the lowering of molecular weight and the increase in higher molecular weight fraction, and consequently the broadening of molecular weight distribution. The lowering of molecular weight may be caused by chain scission and the increase in higher molecular weight fraction by the formation of crosslinks.

Janwattanakul, V. [18] investigated the degradation of photosensitized polyethylene films by natural weathering and accelerated weathering. The change of properties of LDPE and HDPE film sensitized with aromatic ketones and aromatic diketones was investigated. From the results, it was found that the photosensitizers accelerated the degradation. Regarding to the type of photosensitizers, polyethylene films sensitized with thiozanthone, derivatives of benzophenone and of anthraquinone show a higher degradation rate than ones sensitized with benzophenone and anthraquinone. In addition to this, the degradation of high density polyethylene is faster than that of low density polyethylene.

Atorngitjawat P. [19] investigated influence of ultraviolet light on degradation of polyolefin films. Polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE) were exposed to natural weathering and simulated condition in Xenotest Beta lamp machine. It was found that the amount of carbonyl group formation was used as a key indication to report the chemical structure breakdown which increased exponentially as the exposure time increased. The loss of mechanical properties indicates the photo-oxidative degradation time of the films that

became brittle. It was also observed that the degradation rate for PP was fastest and for LDPE was slowest for both exposures.

Pabunruang T. [20] investigated the degradation of prooxidized cassava starch-filled polyethylene films by outdoor exposure and soil burial test. The change of properties of cassava starch-filled polyethylene with/without prooxidant additive was investigated. From the results, it was found that at the high contents of starch in the samples, the degradation rate was high and tensile strength was very low after 6-month exposure. The LDPE films did not change significantly during the outdoor exposure and soil burial test. The films containing the prooxidant lost their properties more than the ones that did not contain such an additive. The amount of starch degraded by the fungi in each formula was directly related to the decreasing properties of the starch-LDPE films.



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CHAPTER III

EXPERIMENTAL

3.1 Materials

High density polyethylene (HDPE) blown film, grade ExxonMobil HTA 001 HD obtained from ExxonMobil Chemical Co., Ltd., was used as the polymeric matrix. The physical and mechanical properties of the materials are listed in Table 3.1.

Table 3.1 Physical mechanical properties ExxonMobil HTA 001 HD

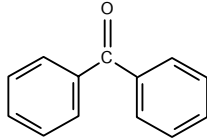
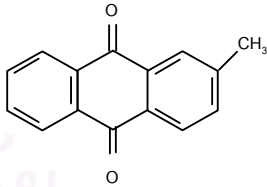
General Properties	Test Method	Unit	Typical Value
Melt Index (21.6kg)	ASTM D 1238	g/10 min	9
Melt Index (2.16kg)	ASTM D 1238	g/10 min	0.07
Density	ASTM D 1505	g/cm ³	0.952
Vicat Softening Point (DSC)	ASTM D 1525	°C	125
Tensile strength at yield (MD/TD)	ASTM D 882	MPa	31/30
Tensile strength at break (MD/TD)	ASTM D 882	MPa	56/56
Elongation at break (MD/TD)	ASTM D 882	MPa	320/530
Elmendorf tear strength (MD/TD)	ASTM D 1922	g	11/58
Dart drop impact	ASTM D 1709	g	170

Calcium carbonate master batch (Calcarb33), supplied by Calcium Products Co., Ltd. was used as filler to catalyze the mechanical degradation of high-density polyethylene. The specifications of calcium carbonate filler are listed in Table 3.2. Photosensitizers are aromatic ketone and aromatic diketone, and their properties are presented in Table 3.3.

Table 3.2 Specification of Calcarb33

General Properties	Test Method	Unit	Typical Value
Melt Index (21.6kg)	ASTM D 1238	g/10 min	2.85
Melt Index (2.16kg)	ASTM D 1238	g/10 min	0.5
Density	ASTM D 1505	g/cm ³	1.85
Water Content	JIS K 5101	%	0.1
Filler Content	500°C/2 hr.	%	75
Polyolefin content	500°C/2 hr.	%	25
Moisture	Karl Fischer	ppm	417

Table 3.3 The character and properties of photosensitizers

Photosensitizer	Appearance	Melting Point (°C)	Boiling Point (°C)	Chemical Structure
Benzophenone (Aromatic Ketone)	White Prisms	48-49	305	
2-Methylantraquinone (Aromatic Diketone)	Yellow powder	177	236-238	

3.2 Film Preparation

The films as composition shown in Table 3.4 were prepared with rolling mixer in the feed hopper. Then the photosensitized calcium carbonate filled HDPE films of average thickness and width of 0.02 ± 0.005 millimeter and 300 millimeter, respectively, were obtained by extruding the mixture in HDPE film blowing machine with an extruder model THIP MT3 02. The temperature of feed, compression 1, compression 2, metering and die zones were 210, 225, 230, 230 and 220 °C, respectively. The films were prepared in rectangular shape, cut to size 300 x 1200 millimeter. The films were fixed on the exposure rack as shown in Figure 3.1

Table 3.4 The composition of photosensitized CaCO₃ filled HDPE film

Sample	Composition (%)			
	HDPE	CaCO ₃	2-Methylantraquinone	Benzophenone
HD/0/0	100	-	-	-
HD/20/0	80	20	-	-
HD/50/0	50	50	-	-
HD/0/0.25A	100	-	0.25	-
HD/20/0.25A	80	20	0.25	-
HD/50/0.25A	50	50	0.25	-
HD/0/0.5A	100	-	0.5	-
HD/20/0.5A	80	20	0.5	-
HD/50/0.5A	50	50	0.5	-
HD/0/0.5B	100	-	-	0.5
HD/20/0.5B	80	20	-	0.5
HD/50/0.5B	50	50	-	0.5
HD/0/1.0B	100	-	-	1.0
HD/20/1.0B	80	20	-	1.0
HD/50/1.0B	50	50	-	1.0

3.3 Outdoor Exposure

Outdoor exposure was carried out under the tropical climate at Banpong, Ratchaburi, Thailand. The meteorological and radiation data were shown in Table 3.5. The exposure racks oriented to the south with the exposure surface inclined at 45° to the horizontal, to get the maximum sunlight (ASTM D 1435-99) as shown in Figure 3.2 [21]. The films were collected every week for 12 weeks since December, 2001 to February, 2002 for chemical characterization and mechanical properties testing.

Table 3.5 Meteorological data

Month	Temperature ($^{\circ}\text{C}$)	Relative Humidity (%)	Rainfall Amount (mm)	UV Radiation (MJ/m^2)
December 2001	25.0	75.0	0.9	0.6092
January 2002	25.0	72.0	0.0	0.5740
February 2002	27.9	72.0	0.0	0.6168

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Figure 3.1 The exposure rack



Figure 3.2 The exposure racks for outdoor exposure

3.4 Properties Measurement

3.4.1 Tensile Strength and Elongation

The samples were collected at an interval for mechanical testing. According to the ASTM D 882-99, the specimens for tensile testing were cut out along the machine direction, into strip of 25.4 mm wide with a gauge length of 50 mm. Tensile strength was measured by means of INSTRON tensile tester model 5583 with cross head speed of 100 mm/min at the test condition of $27 \pm 2^{\circ}\text{C}$ and $65 \pm 2\%$ relative humidity. The thicknesses of test specimens were measured with a thickness gauge to the nearest 0.001 mm. An average of five specimens was reported as a representative value. The resulting stress-strain traces were determined as an average. The tensile strength (σ) was calculated as: [22]

$$\sigma = F/A \quad (3.1)$$

where σ = Tensile strength at break, MPa

F = Load at break, N

A = Cross section area of specimen, mm^2

The elongation at break was calculated as follows:

$$\% \varepsilon = (L-L_0)/L_0 \times 100 \quad (3.2)$$

where $\% \varepsilon$ = Elongation at break, %

L = Stretched length at break of sample, cm

L_0 = Original length of the specimen (gauge length), cm

3.4.2 Molecular Weight Measurements

Molecular weight of HDPE was determined by the viscosity method, using decahydronaphthalene solution and calculated from the Mark-Houwink-Sakurada equation: [23]

$$[\eta] = kM^a \quad (3.3)$$

where $[\eta]$ = intrinsic viscosity
 M = viscosity average molecular weight
 k^* = 62.0×10^{-3} ml/g
 a^* = 0.70

Constants k^* and a^* , can be obtained from the literature for a given polymer-solvent system [24]

Approximately 15 ml of decahydronaphthalene was transferred by a syringe into an Ubbelohde viscometer (SHOTT No. 50110), which is permanently positioned in the oil bath which was kept at constant given temperature until the solution attained thermal equilibrium (about 5 min). The liquid level was brought about approximately 10 mm above the upper graduation mark in the viscometer capillary. As the meniscus passed this point, the timer was started and the interval for the solution to drain to the lower mark in the capillary was tuned. The efflux time of the solution was measured at least three times. Three consecutive reading should agree within 0.2 second. The solution was then removed from the viscometer.

The samples were weighed about 0.04 g and dissolved with hot decahydronaphthalene. The solution was made up to 50 ml mark with solvent maintained at given temperature by means of a syringe and the flask was shaken once again. In the same manner as decahydronaphthalene, three consecutive efflux times of the first PE solution in the viscometer were recorded. The first PE solution was then diluted by adding 15, 10 and 5 ml of the first solution into the three 25 ml volumetric flask respectively, and then all solution were made up to the 25 ml mark with the solvent maintained at given temperature.

3.4.3 Carbonyl Index Measurements

The FTIR adsorption spectra of HDPE films were recorded on an FTIR a spectrophotometer Perkin-Elmer model 1760X and were used for estimating the changes in carbonyl group C=O in the chain at 1715 cm^{-1} . The polyethylene band at 1465 cm^{-1} was served as an internal standard to which the absorbances of the other bands were related. The results were expressed by the carbonyl index defined as follows: [15]

$$I_{\text{CO}} = A_{1715} / A_{1465} \quad (3.4)$$

where I_{CO} = Carbonyl Index
 A_{1715} = Absorbance of the carbonyl group
 A_{1465} = Internal standard band in HDPE chain

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CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Calcium Carbonate and Photosensitizers on HDPE Films

The tensile strength and elongation at break of unexposed composite HDPE films are shown in Table 4.1.

From Figure 4.1, the tensile strength of unsensitized filled HDPE film does not change significantly (29.7-31.5 MPa) with increasing calcium carbonate content (20-50%). The proportion of calcium carbonate of 20% in unsensitized HDPE film is suitable. The tensile strength of unsensitized 50% CaCO₃ filled HDPE film does not increase. The combination of calcium carbonate and plastic polymer is stress-induced reaction, a field commonly called mechanochemistry. Macroradicals are generated and can be terminated by oxygen in air, leading to the introduction of polar groups onto polymer chains. Introduction of polar groups can assist in the enhancement of tensile strength.

The elongation at break decreases with increasing calcium carbonate content. The calcium carbonate affects the elongation at break of unsensitized filled HDPE films according to their moisture absorbing characteristic and interfacial bonding. The calcium carbonate can easily absorb moisture in atmosphere. When heat is applied during processing, the water in calcium carbonate particles evaporates and causes air bubbles to form within the plastic mixture when it is cooled. The air bubbles cause the decrease of the elongation at break of the films.

From Figure 4.2, the tensile strength of sensitized unfilled HDPE films increases with increasing photosensitizer content. The tensile strength of sensitized filled HDPE films decreases with increasing photosensitizer content. The 2-methylantraquinone sensitized samples exhibit lower tensile strength than films sensitized with benzophenone. Elongation at break of sensitized samples decreases with increasing calcium carbonate content. The 2-methylantraquinone sensitized films exhibit lower elongation at break than films sensitized with benzophenone.

Table 4.1 Tensile properties of unexposed composite HDPE films at various contents of calcium carbonate and photosensitizers

Sample	Tensile Strength (MPa)	Elongation at break (%)
HD/0/0	29.7	270.9
HD/20/0	31.5	130.1
HD/50/0	29.8	52.3
HD/0/0.25A	31.2	145.6
HD/20/0.25A	28.2	82.3
HD/50/0.25A	25.3	76.1
HD/0/0.5A	37.1	299.5
HD/20/0.5A	27.1	141.7
HD/50/0.5A	27.7	105.6
HD/0/0.5B	38.6	280.3
HD/20/0.5B	33.9	155.6
HD/50/0.5B	29.0	145.6
HD/0/1.0B	42.2	385.0
HD/20/1.0B	31.7	222.8
HD/50/1.0B	27.6	81.2

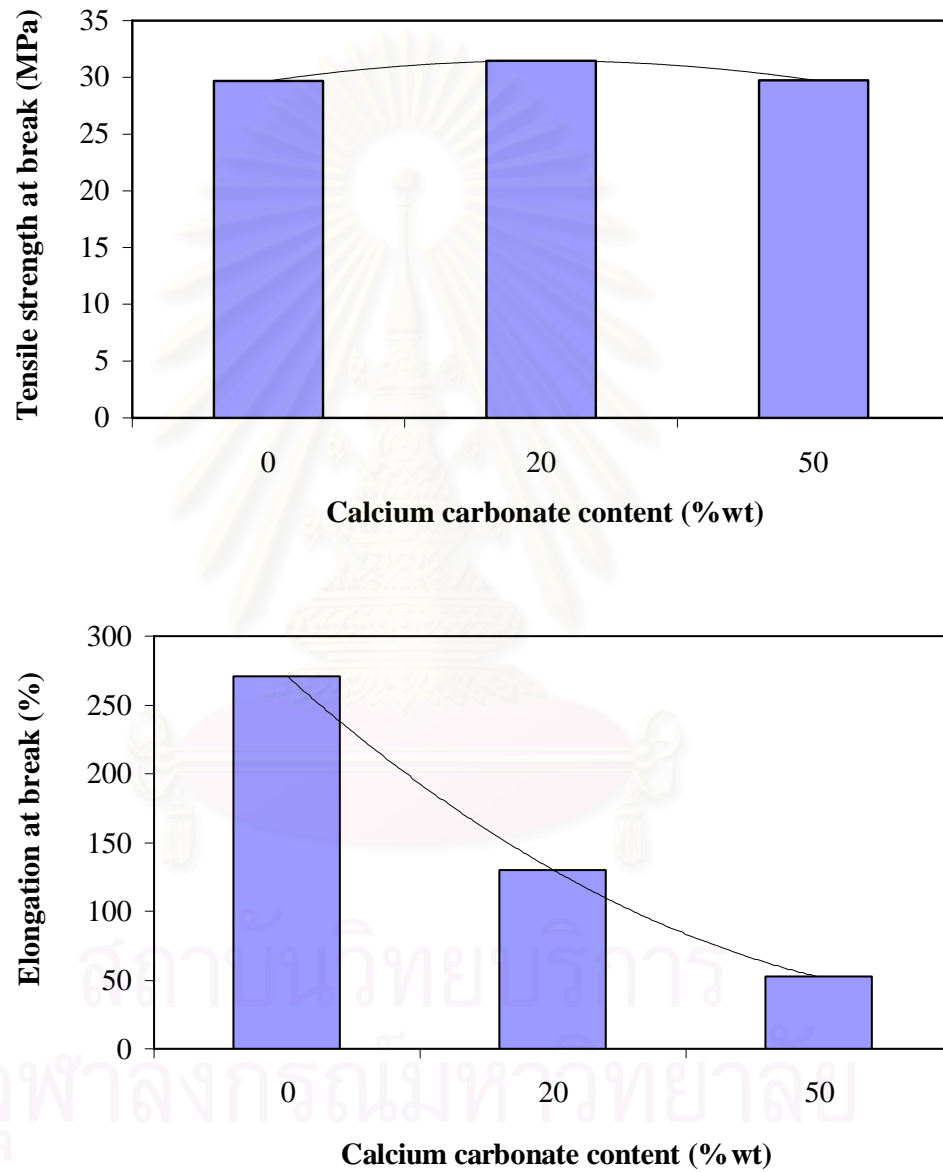


Figure 4.1 Effect of calcium carbonate content on tensile properties of composite HDPE films

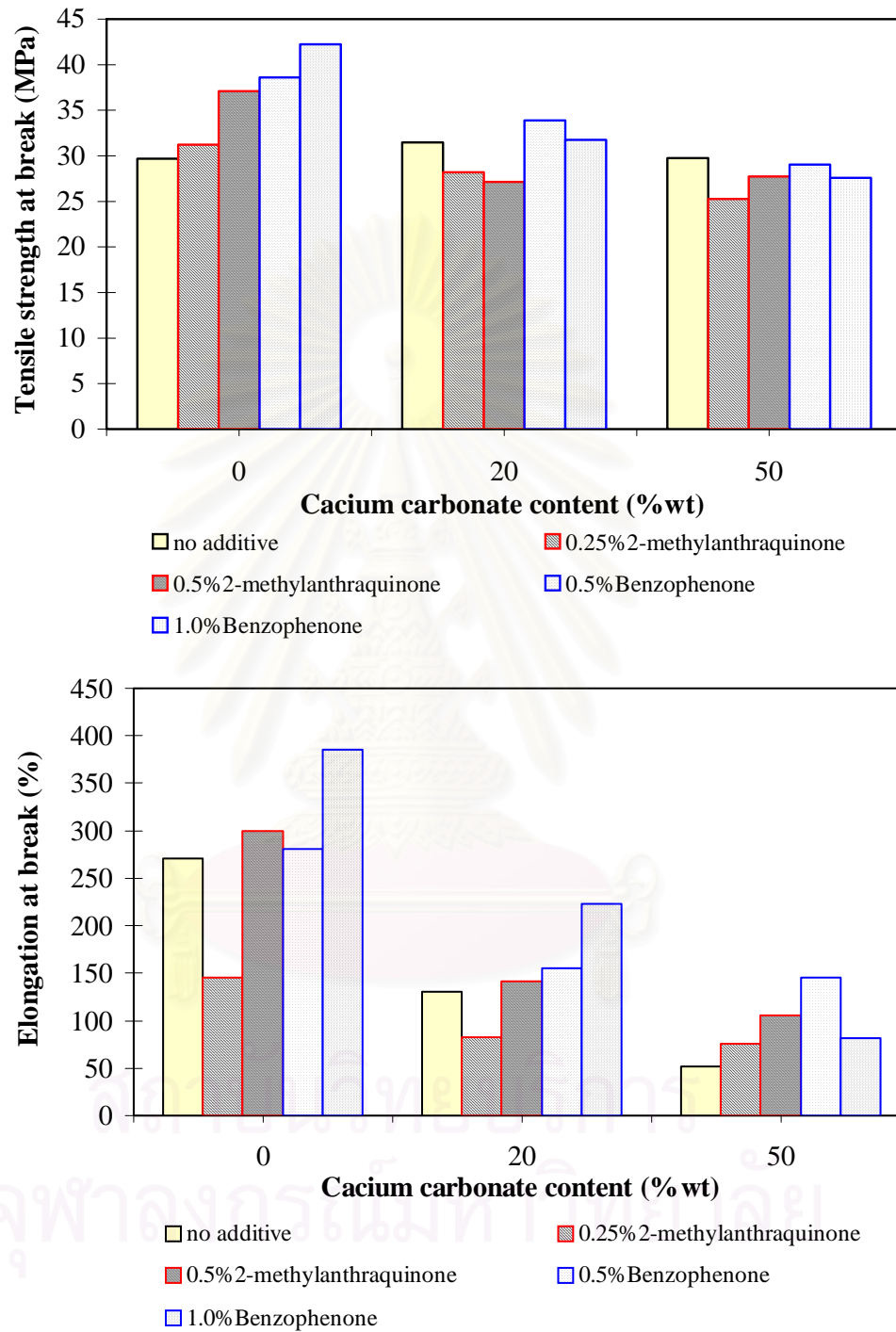


Figure 4.2 Effect of photosensitizer and calcium carbonate content on tensile properties of composite HDPE films

4.2 Degradation of Photosensitized Calcium Carbonate Filled HDPE Film

The activity of photosensitizer and calcium carbonate in HDPE degradation was studied by outdoor exposure. The environmental degradation of photosensitized calcium carbonate filled HDPE films was studied for 12-week outdoor exposure. The films were exposed in such way that the main part of film was free from the obstruction. The average temperature, relative humidity, rainfall amount and ultraviolet irradiation data are shown in Table 3.5. The degradation of composite polyethylene films was followed by measuring tensile properties, molecular weight and infrared spectra.

4.2.1 Tensile Properties Measurement

Tables 4.2 and 4.3 show the tensile properties of the exposed composite HDPE films.

From Figure 4.3, the tensile properties (tensile strength and elongation at break) of unsensitized filled HDPE films decrease faster than unsensitized unfilled HDPE film. The tensile properties of unsensitized 50% CaCO₃ filled HDPE film decrease faster than unsensitized 20% CaCO₃ filled HDPE film.

From Figure 4.4a, the tensile strength of the 0.25% 2-methylantraquinone sensitized unfilled HDPE films and the 0.25% 2-methylantraquinone sensitized filled HDPE films decrease to low value during outdoor expose. The tensile strength of 0.25% 2-methylantraquinone sensitized 50% CaCO₃ filled HDPE film decreases to zero within 6 weeks. The tensile strength of 0.25% 2-methylantraquinone sensitized 20% CaCO₃ filled HDPE film and the 0.25% 2-methylantraquinone sensitized unfilled HDPE film decrease to zero within 10 weeks and 12 weeks respectively.

From Figure 4.4b, the tensile strength of the 0.5% 2-methylantraquinone sensitized unfilled HDPE films and the 0.5% 2-methylantraquinone sensitized filled HDPE films exhibit similar behavior as films with 0.25% sensitizer. The 0.5% 2-methylantraquinone sensitized samples show the rate of decreasing tensile strength faster than that of 0.25% 2-methylantraquinone

sensitized samples. For the increase of sensitizer content (from 0.25 to 0.5%) the time of decreasing tensile strength to zero value changes from 12 weeks to 10 weeks, 10 weeks to 8 weeks and no change for sensitized unfilled HDPE film, sensitized 20% CaCO₃ filled HDPE film and sensitized 50% CaCO₃ filled HDPE film, respectively.

From Figure 4.5a, the 0.25% 2-methylantraquinone sensitized 50% CaCO₃ filled HDPE film shows the rate of decreasing elongation at break faster than that of 0.25% 2-methylantraquinone sensitized 20% CaCO₃ filled HDPE film and that of 0.25% 2-methylantraquinone sensitized unfilled HDPE film. The elongation at break decreases to zero value within 4 weeks, 6 weeks and 8 weeks for sensitized 50% CaCO₃ filled HDPE film, sensitized 20% CaCO₃ filled HDPE film and sensitized unfilled HDPE film. Elongation at break decreases with increasing photosensitizers content from 0.25% to 0.5%. The 0.5% 2-methylantraquinone sensitized films exhibit the rate of decreasing elongation faster than those with 0.25% 2-methylantraquinone.

From Figure 4.5b, the time of decreasing elongation at break to zero value are 2 weeks, 4 weeks and 6 weeks for 50% CaCO₃ filled HDPE film, 20% CaCO₃ filled HDPE film and unfilled HDPE film, (0.5 % sensitizer) respectively.

From Figure 4.6a, the tensile strength of the 0.5% benzophenone sensitized 50% CaCO₃ filled HDPE film decreases faster than that of the 0.5% benzophenone sensitized 20% CaCO₃ filled HDPE film and the 0.5% benzophenone sensitized unfilled HDPE film.

From Figure 4.6b, the tensile strength of the 1.0% benzophenone sensitized unfilled HDPE film and filled HDPE film exhibit similar behavior as film with 0.5% sensitizer. The tensile strength of 1.0% benzophenone sensitized film decrease faster than that of 0.5% benzophenone sensitized unfilled HDPE film and filled HDPE film. For different photosensitizers, samples sensitized with 2-methylantraquinone shows the higher degradation rate than films sensitized with benzophenone.

From Figure 4.7, the increasing photosensitizer content does not affect the elongation at break for both unfilled and CaCO₃ filled films. For different photosensitizers, samples sensitized with 2-methylantraquinone show the higher degradation rate than films sensitized with benzophenone.

Table 4.2 Tensile strength of composite HDPE films during outdoor exposure

Sample	Tensile Strength (MPa)					
	Outdoor exposure time (weeks)					
	2	4	6	8	10	12
HD/0/0	25.7	24.3	25.0	24.5	25.0	25.0
HD/20/0	27.8	21.6	26.2	26.0	24.0	20.8
HD/50/0	25.0	19.1	17.1	16.2	10.6	7.7
HD/0/0.25A	22.6	21.5	16.2	6.9	8.2	0.0
HD/20/0.25A	21.9	12.3	6.1	7.0	0.0	0.0
HD/50/0.25A	9.8	6.9	0.0	0.0	0.0	0.0
HD/0/0.5A	25.9	9.4	7.2	12.3	0.0	0.0
HD/20/0.5A	14.6	7.0	5.7	0.0	0.0	0.0
HD/50/0.5A	8.1	3.4	0.0	0.0	0.0	0.0
HD/0/0.5B	27.5	24.4	26.6	25.0	25.1	23.7
HD/20/0.5B	26.1	23.2	25.2	25.2	22.3	19.2
HD/50/0.5B	23.0	18.3	17.2	16.8	13.5	11.2
HD/0/1.0B	29.2	25.2	24.7	25.8	26.1	25.0
HD/20/1.0B	25.0	24.9	24.0	21.3	21.1	17.1
HD/50/1.0B	22.9	20.1	16.3	11.6	9.2	7.2

Table 4.3 Elongation at break of composite HDPE films during outdoor exposure

Sample	Elongation at break (%)					
	Outdoor exposure time (weeks)					
	2	4	6	8	10	12
HD/0/0	226.7	244.5	169.5	228.9	116.7	113.4
HD/20/0	75.6	35.1	25.0	11.4	6.2	3.9
HD/50/0	29.9	10.6	3.9	3.9	1.2	0.9
HD/0/0.25A	130.1	7.0	3.9	1.0	1.0	0.0
HD/20/0.25A	15.7	2.4	0.9	0.9	0.9	0.0
HD/50/0.25A	1.4	0.9	0.0	0.0	0.0	0.0
HD/0/0.5A	17.2	1.9	0.9	0.0	0.0	0.0
HD/20/0.5A	2.4	0.9	0.9	0.0	0.0	0.0
HD/50/0.5A	1.0	0.9	0.0	0.0	0.0	0.0
HD/0/0.5B	244.5	163.9	114.5	96.7	62.2	21.0
HD/20/0.5B	69.5	25.0	21.0	10.1	6.3	3.8
HD/50/0.5B	28.9	7.9	4.6	3.9	2.6	1.7
HD/0/1.0B	346.7	237.3	184.5	115.6	77.8	46.1
HD/20/1.0B	124.5	84.5	24.9	6.3	6.4	3.4
HD/50/1.0B	18.1	8.6	3.9	7.2	2.3	1.7

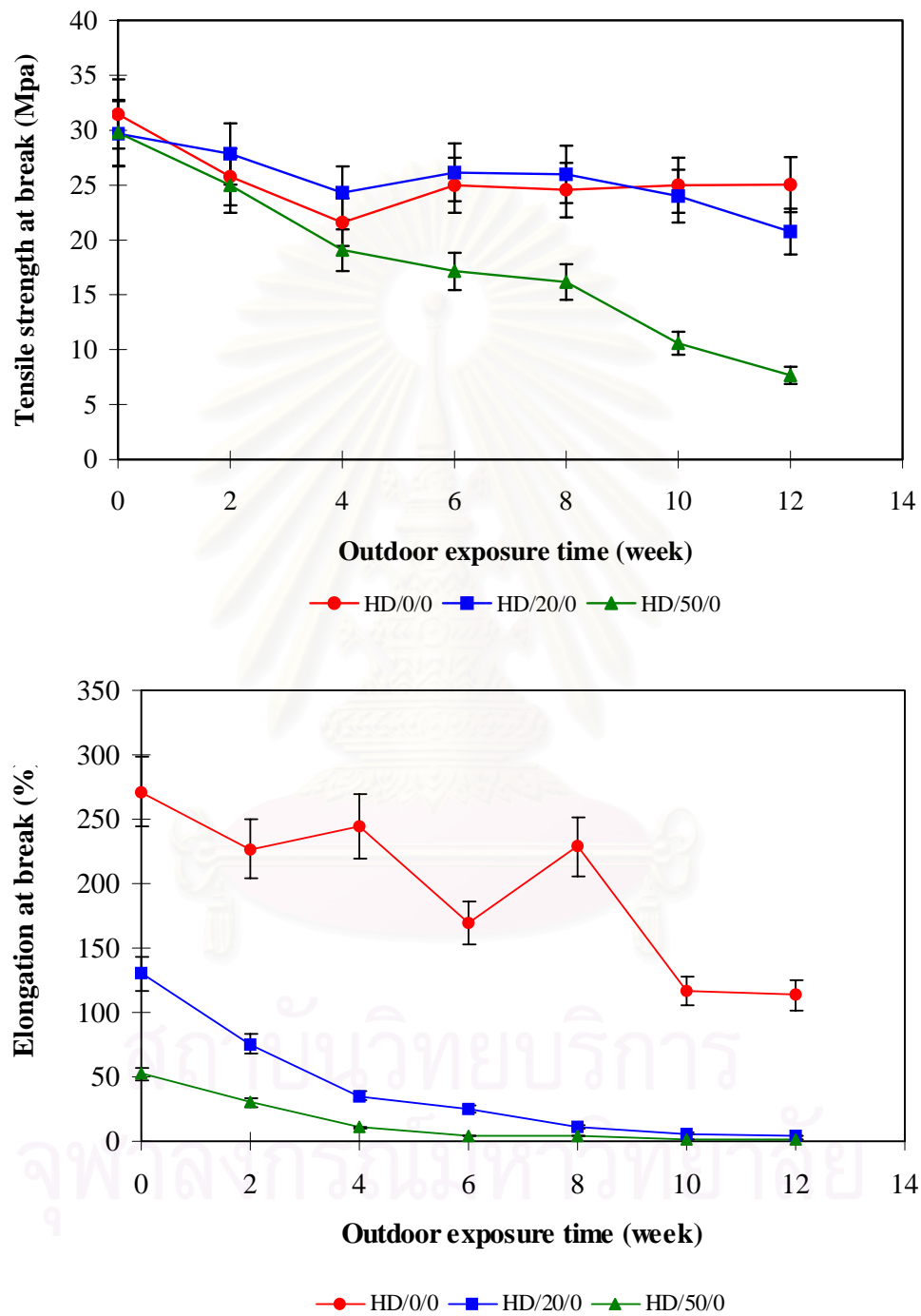


Figure 4.3 Tensile properties of unsensitized unfilled HDPE films and unsensitized filled HDPE films during natural weathering

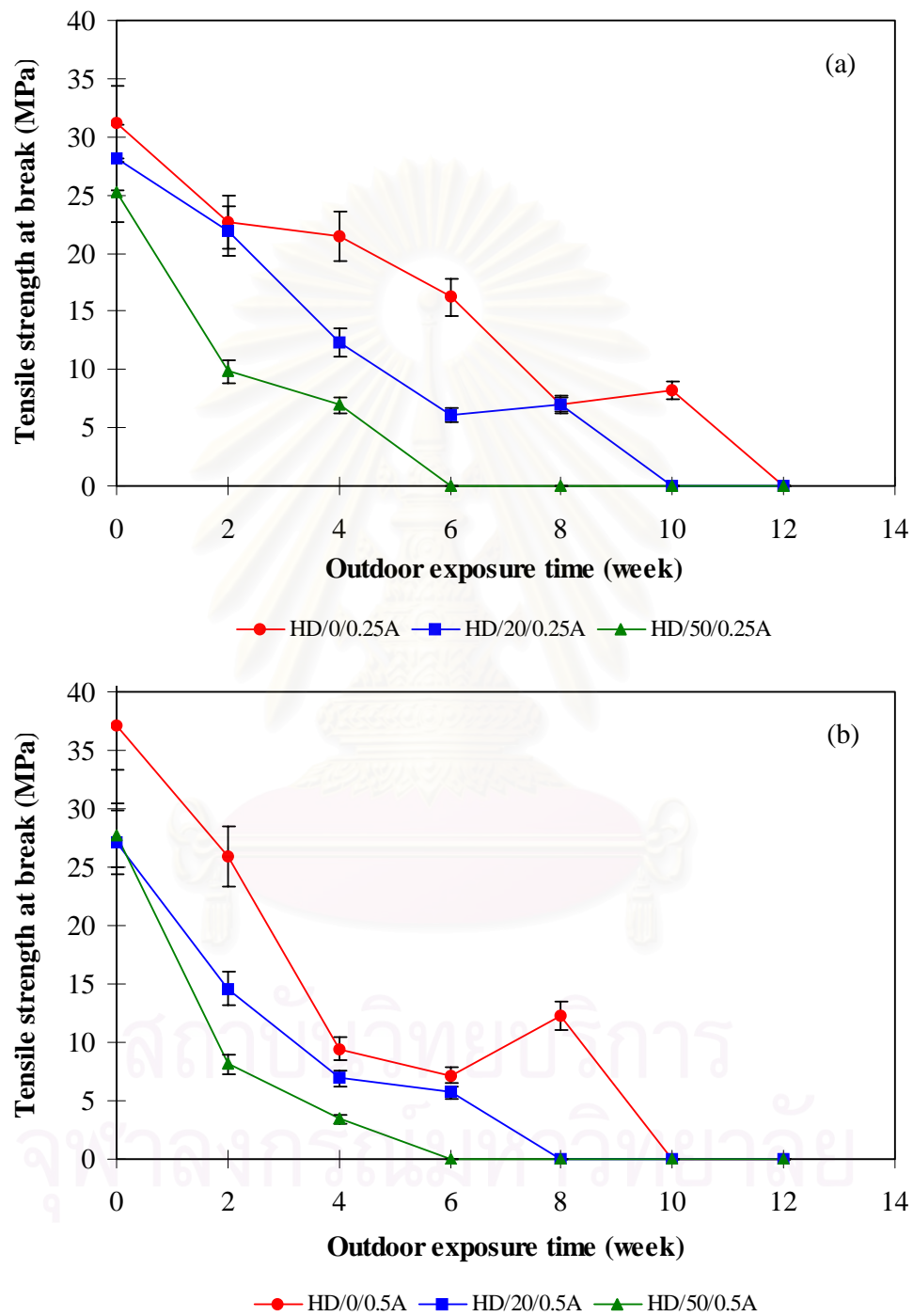


Figure 4.4 Tensile strength at break of 0.25% 2-methylanthraquinone (a) and 0.5% 2-methylanthraquinone (b) sensitized unfilled HDPE films and sensitized filled HDPE films during natural weathering

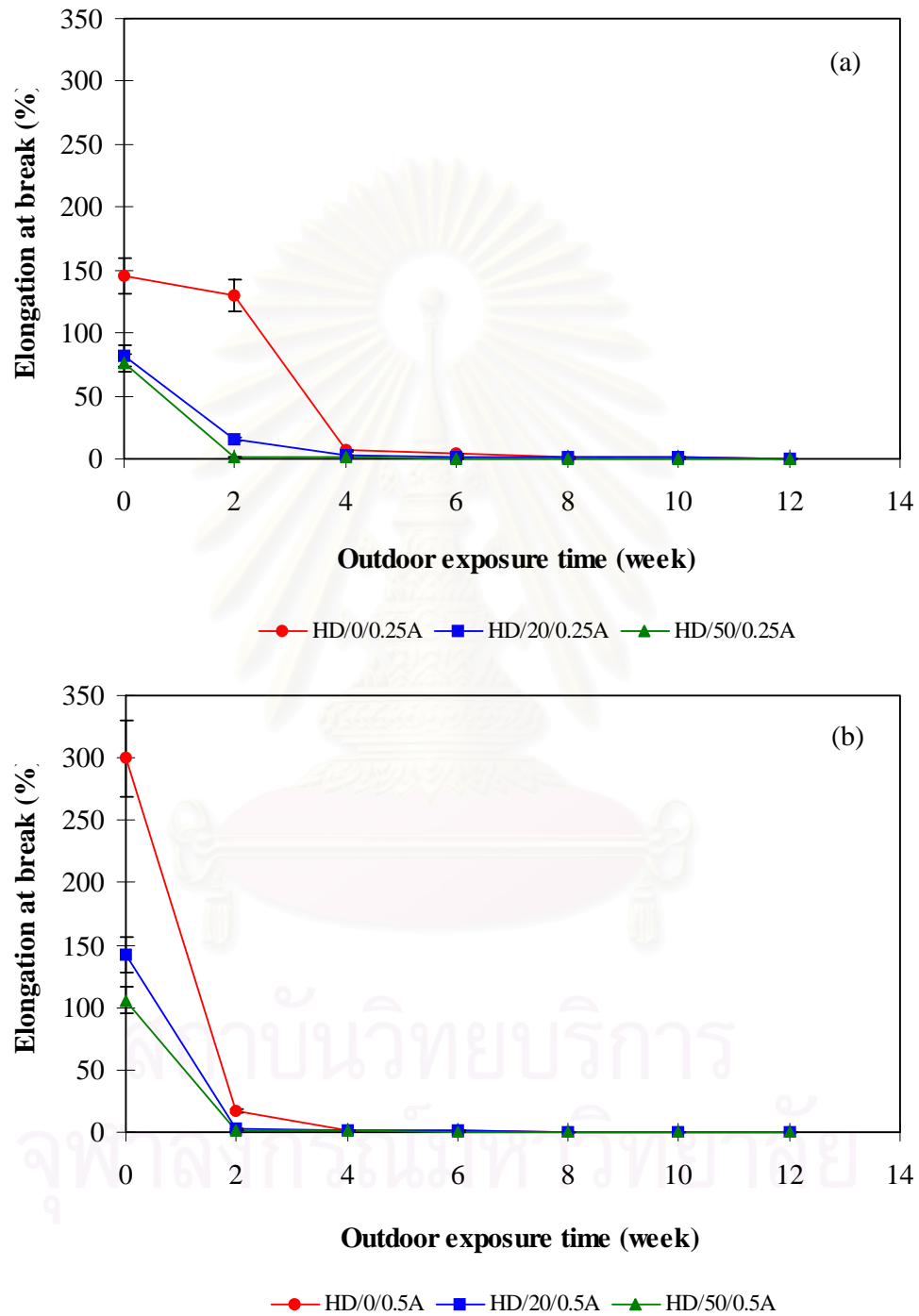


Figure 4.5 Elongation at break of 0.25% 2-methylanthraquinone (a) and 0.5% 2-methylanthraquinone (b) sensitized unfilled HDPE films and sensitized filled HDPE films during natural weathering

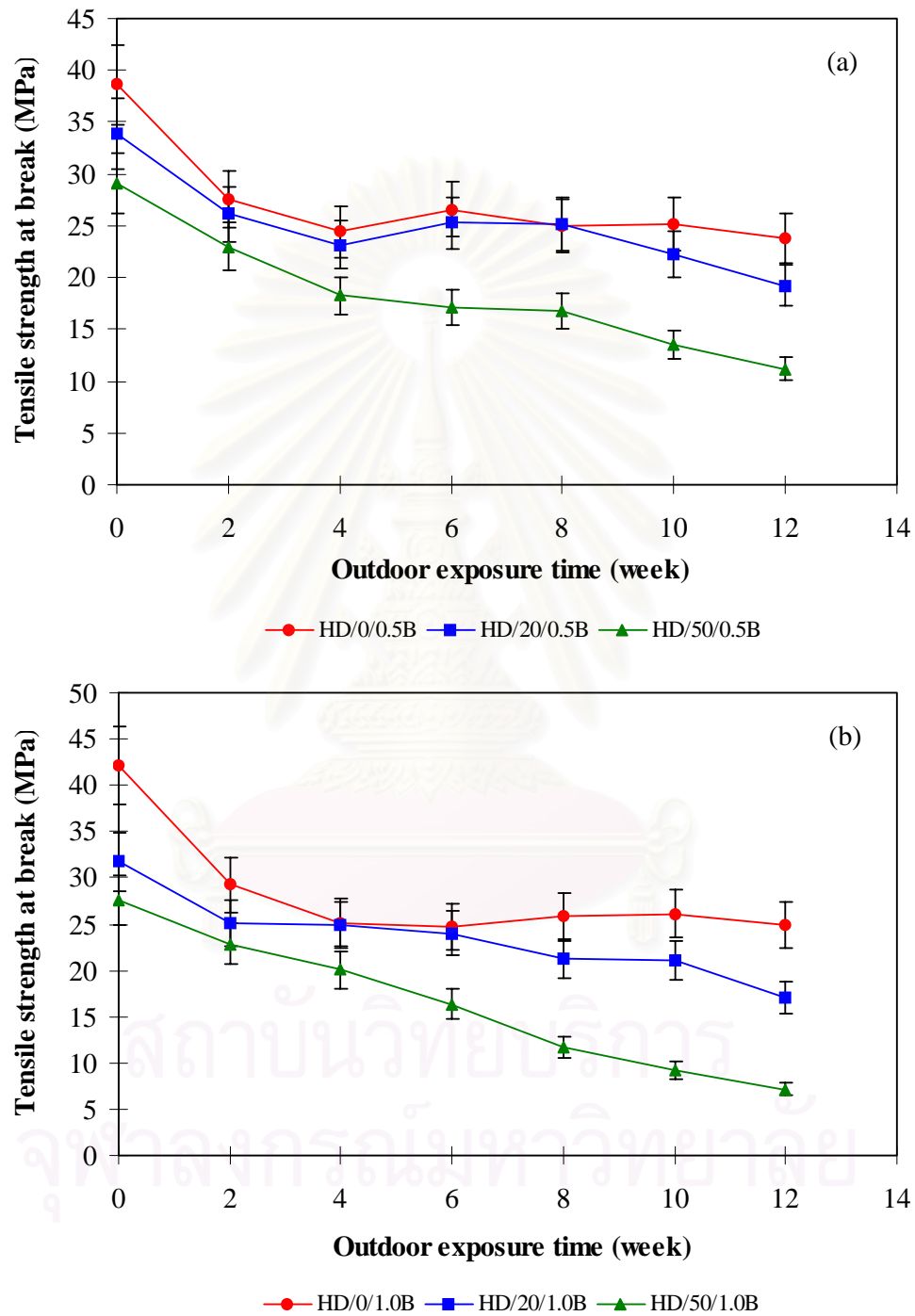


Figure 4.6 Tensile strength at break of 0.5% benzophenone (a) and 1.0% benzophenone (b) sensitized unfilled HDPE films and sensitized filled HDPE films during natural weathering

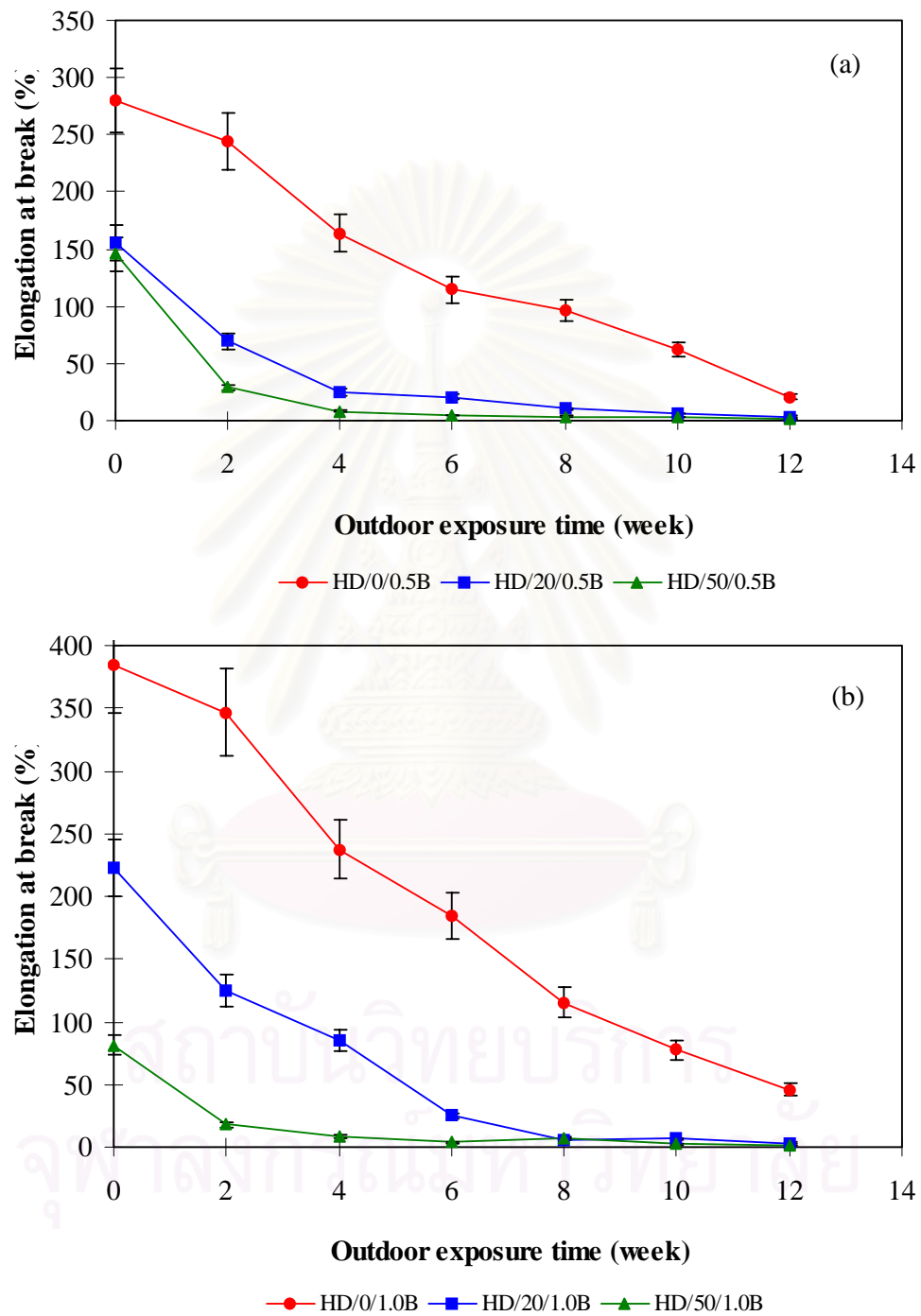


Figure 4.7 Elongation at break of 0.5% benzophenone (a) and 1.0% benzophenone (b) sensitized unfilled HDPE films and sensitized filled HDPE films during natural weathering

4.2.2 Molecular Weight Measurement

Regarding molecular weight determination, it is found that the exposed samples contain insoluble material, caused by the formation of crosslinking of polymer chains which improves heat stability and solvent resistance. The change of intrinsic viscosity and molecular weight of HD/0/0, HD/20/0, HD/0/0.25A, HD/20/0.25A, HD/0/1.0B and HD/20/1.0B before and after 12-week outdoor exposure are shown in Table 4.4 and Figure 4.8.

From Figure 4.8, when the exposure proceeds, the molecular weights of all samples decrease. The molecular weights of all sensitized samples decrease more than all unsensitized samples. The molecular weight of the 0.25% 2-methylanthraquinone sensitized film (23,430) decreases more than that of 1.0% benzophenone sensitized samples (40,420), corresponding to a sharp drop of tensile properties. The molecular weight of sensitized and filled films, HD/20/0.25A and HD/20/1.0B drop to 17,550 and 24,380, respectively. The molecular weight of sensitized unfilled HDPE films, sensitized filled HDPE films and unsensitized filled HDPE film decreases rapidly with time and after 12-week outdoor exposure, it reaches about 1/8-1/9 time of the initial molecular weight.

Table 4.4 Change in intrinsic viscosity and molecular weight of unexposed and exposed composite HDPE films after 12-week outdoor exposure

Samples	Intrinsic viscosity (η)			Molecular weight $\times 10^3$ (M_n)		
	Original	12 weeks	%Difference	Original	12 weeks	%Decrease
HD/0/0	3.10	2.69	13.2	192.42	157.12	18.3
HD/20/0	2.06	0.46	77.7	107.32	12.60	88.3
HD/0/0.25A	2.95	0.71	75.9	179.26	23.43	86.9
HD/20/0.25A	2.32	0.58	75.0	127.18	17.55	86.2
HD/0/1.0B	2.93	1.04	64.5	177.52	40.42	77.2
HD/20/1.0B	2.31	0.73	68.4	126.40	24.38	80.7

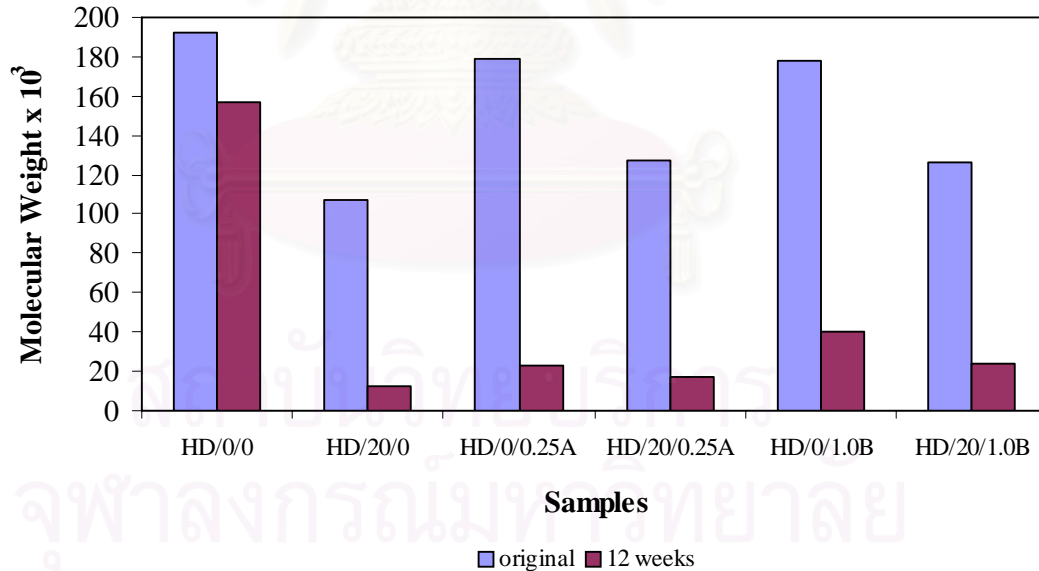


Figure 4.8 Molecular weight of unexposed and exposed composite HDPE films after 12-week outdoor exposure

4.2.3 Fourier Transform Infrared Absorption Measurement

The FTIR method offers valuable information concerning chemical changes produced in composite HDPE films. The IR vibrations of high-density polyethylene and calcium carbonate are shown in Table 4.5. Spectra of the HD/0/0 and HD/20/0 films are shown in Figures 4.9 and 4.10.

In the FTIR spectra of composite HDPE films, the peaks of importance are:

(1) The polyethylene band at 1462 cm^{-1} served as an internal standard to which the absorbances of the other bands were related.

(2) The 1715 cm^{-1} band corresponding to the presence of the carbonyl group in the exposed and degraded polyethylene chain

Spectra of the HD/0/0, HD/20/0, HD/0/0.25A, HD/20/0.25A, HD/0/1.0B and HD/20/1.0B films before and after 12-week outdoor exposure are shown in Figures 4.11-4.16.

From Figures 4.11-4.16, it can be seen that the composites HDPE film generate carbonyl group after 12-week outdoor exposure. The 2-methylantraquinone sensitized 20% calcium carbonate filled HDPE film generates most carbonyl group.

Corresponding to a carbonyl index in Table 4.6 and Figure 4.17, the increasing percentage of carbonyl index of unsensitized samples does not change significantly (1-4%) with increasing calcium carbonate content (20%). The change in the carbonyl index of 2-methylantraquinone sensitized 20% CaCO_3 filled HDPE film before and after exposure is about 20%. The benzophenone sensitized films exhibit lower increasing percentage of carbonyl index than films sensitized with 2-methylantraquinone.

Table 4.5 Infrared vibrations and assignments for high-density polyethylene film and calcium carbonate

Major IR bands		
Samples	Frequency (cm^{-1})	Assignment
HDPE	2916, 2851 (s)	C-H stretching
	1462 (m)	CH ₂ scissoring and asym bending
	719 (m)	CH ₂ rocking
CaCO ₃	1797 (s)	C=O stretching
	1430 (s,br)	C-H scissoring
	875 (m)	C-H stretching
	712 (m)	CH ₂ rocking

m = medium, s = strong, br = broad

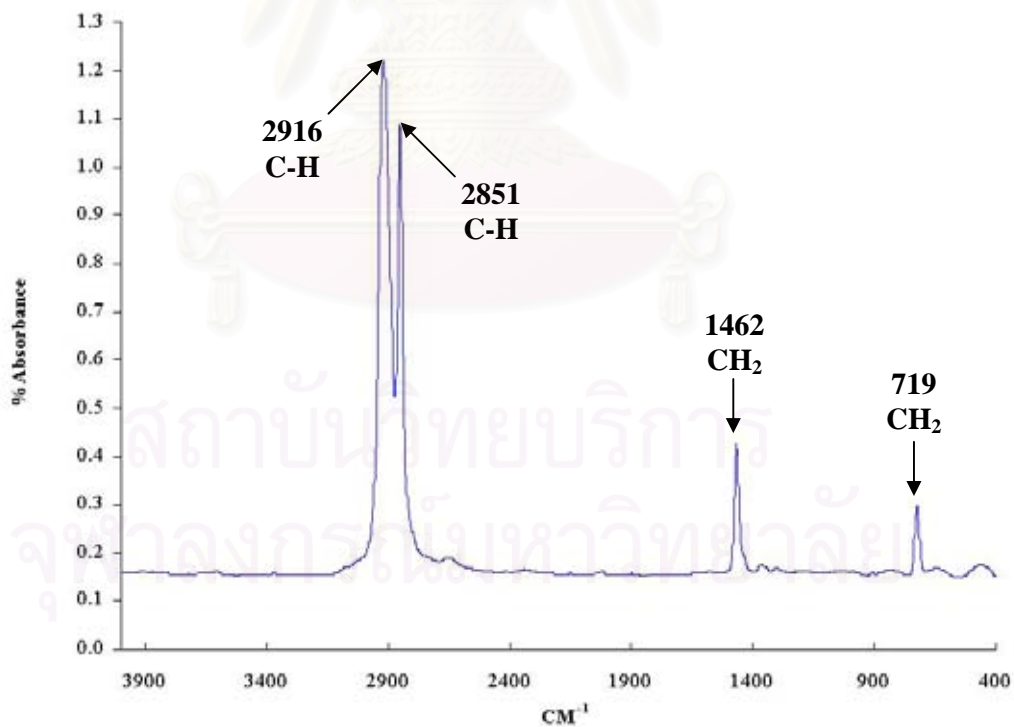


Figure 4.9 FTIR spectrum of HDPE film (Unexposed film)

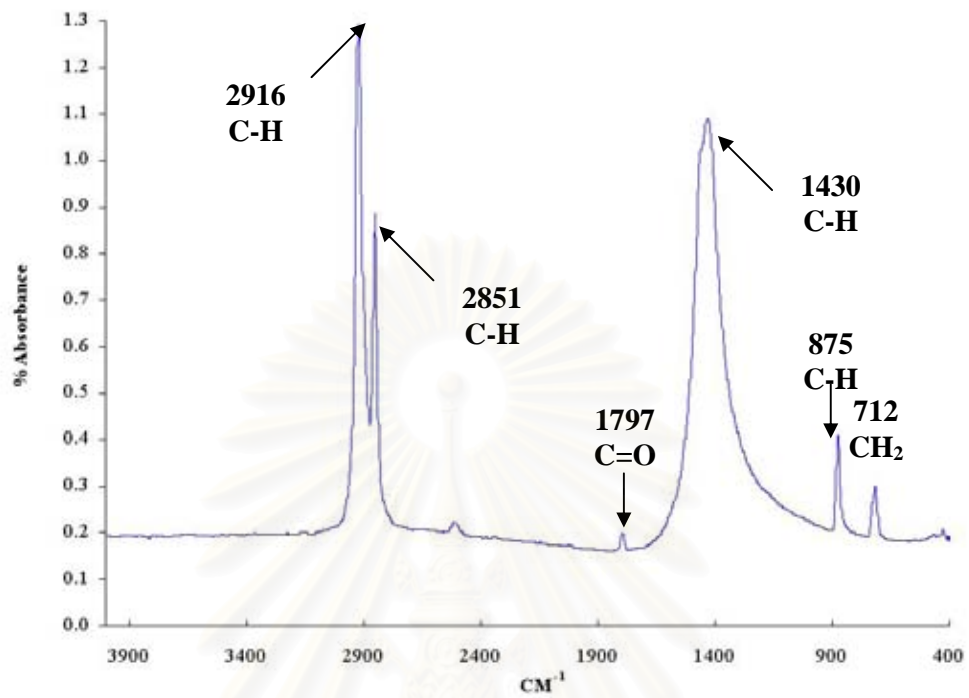


Figure 4.10 FTIR spectrum of 20% CaCO₃ filled HDPE (Unexposed film)

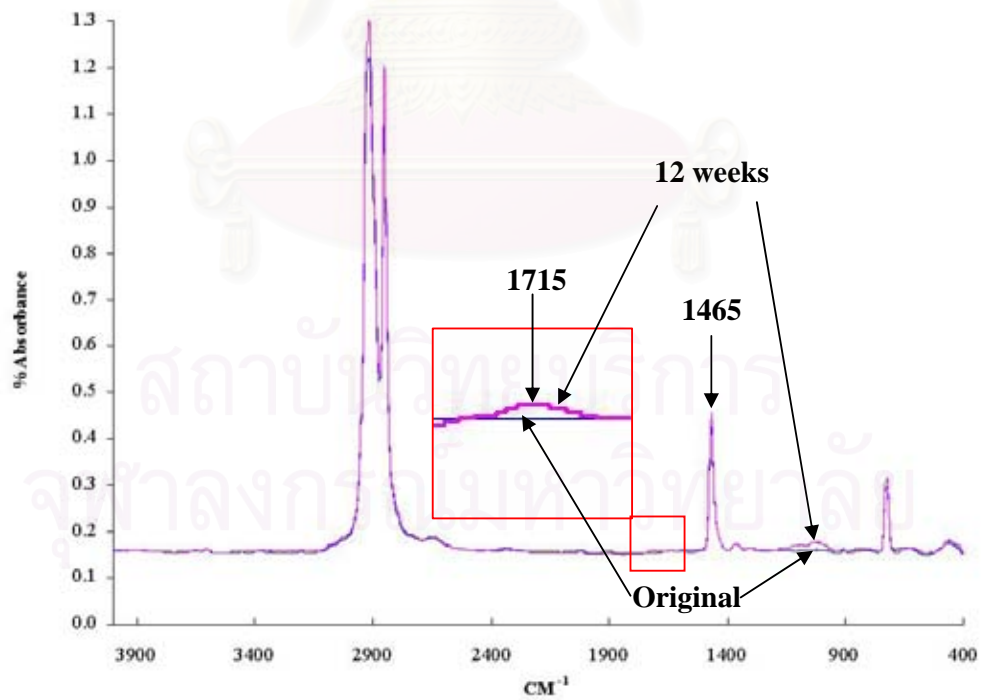


Figure 4.11 FTIR spectra of original and outdoor exposed HDPE films

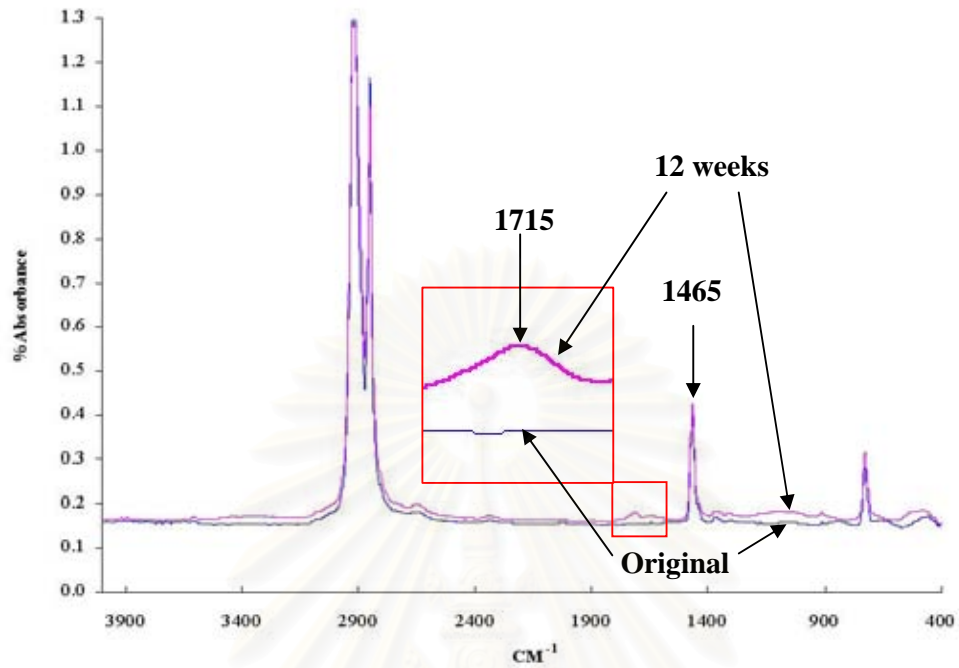


Figure 4.12 FTIR spectra of original and outdoor exposed 0.25% 2-methylantraquinone sensitized HDPE films

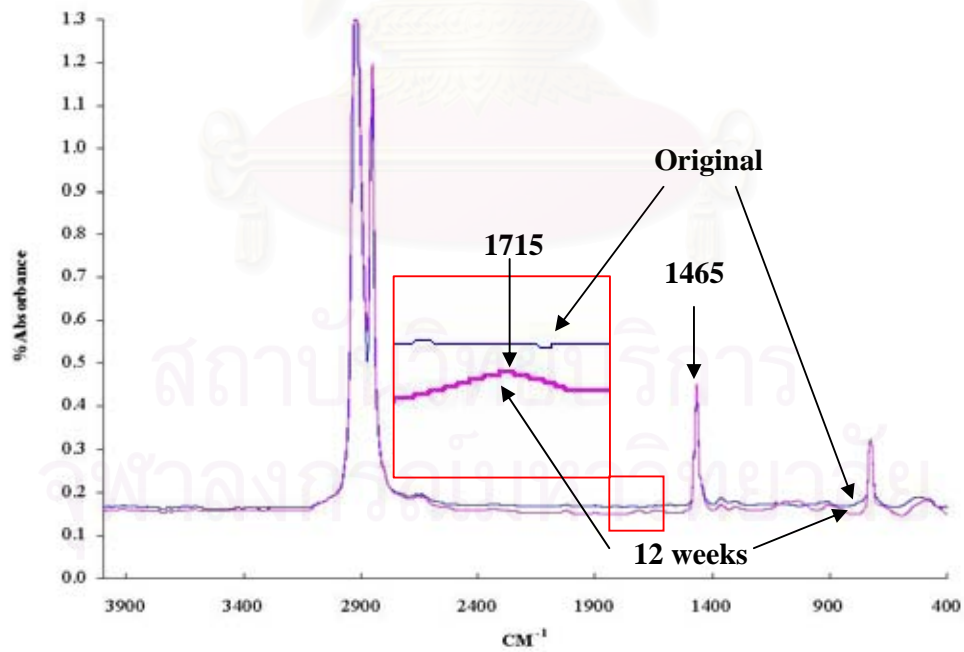


Figure 4.13 FTIR spectra of original and outdoor exposed 1.0% benzophenone sensitized HDPE films

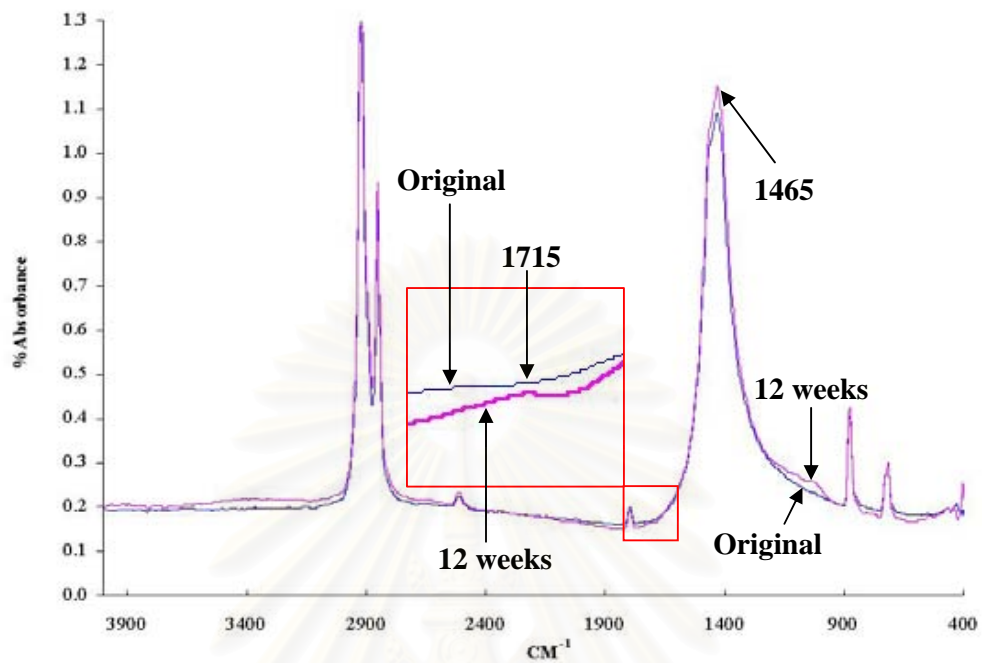


Figure 4.14 FTIR spectra of original and outdoor exposed unsensitized 20% CaCO₃ filled HDPE films

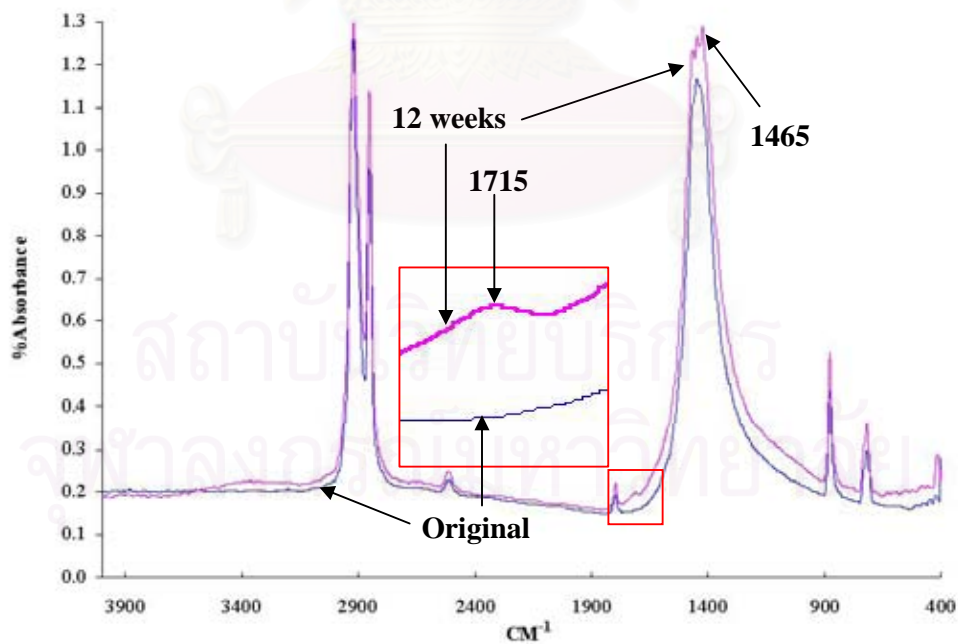


Figure 4.15 FTIR spectra of original and outdoor exposed 0.25% 2-methylantraquinone sensitized 20% CaCO₃ filled HDPE film

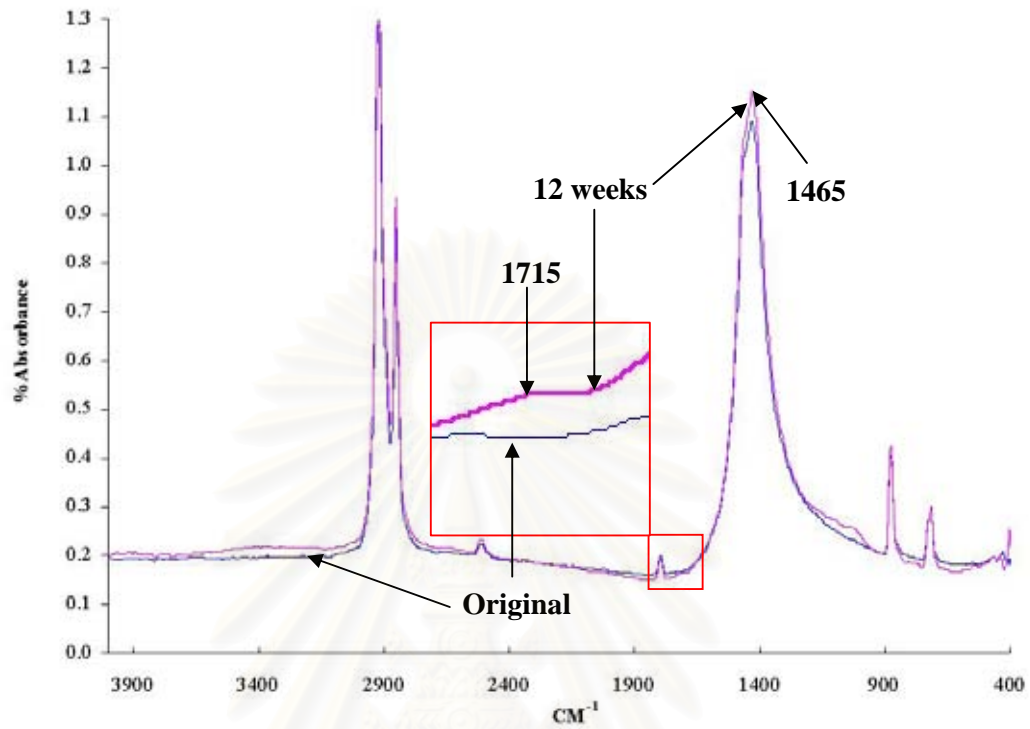


Figure 4.16 FTIR spectra of original and outdoor exposed 1.0% benzophenone sensitized 20% CaCO₃ filled HDPE films

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Table 4.6 Change in the carbonyl indexes of unexposed and exposed composite HDPE films after 12-week outdoor exposure

Exposure time	Carbonyl Index (I_{CO})					
	HD/0/0	HD/20/0	HD/0/0.25A	HD/20/0.25A	HD/0/1.0B	HD/20/1.0B
Original	0.97	0.97	0.97	0.95	0.96	0.91
12 weeks	1.01	0.98	1.09	1.14	1.00	0.97
%Increase	4.1	1.0	12.4	20.0	4.2	6.6

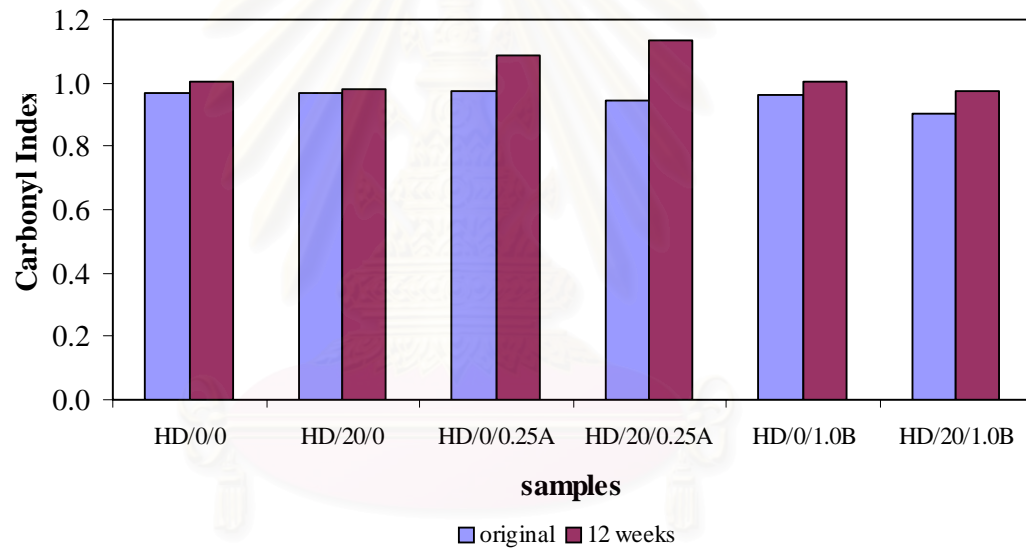


Figure 4.17 The carbonyl indexes of unexposed and exposed composite HDPE films after 12-week outdoor exposure

4.3 Comparison of the Degradation Tendencies in Outdoor Exposure

For comparison of the degradation rate in exposed samples, the value of exposure period is determined when elongation at break is reduced by half. Kubota, H., et al. reported that the elongation at break was suitably used to evaluate the weatherability of plastics. The same idea was applied to evaluate the relationship between unsensitized and sensitized samples and then accelerating factor, A_1 , was obtained

$$A_1 = \frac{t_{1/2}(0)}{t_{1/2}(i)} \quad (4.1)$$

where

$t_{1/2}(0)$ = The period for character to decrease by half of original unsensitized sample

$t_{1/2}(i)$ = The period for character to decrease by half of unsensitized sample

From Table 4.7, Figure 4.18 and Figure 4.19, it can be concluded that the 0.5% 2-methylantraquinone causes the accelerative degradation of unfilled HDPE film, ($A = 9.6$) as well as the 20% CaCO_3 filled HDPE film.

For 0.25% 2-methylantraquinone film, the sensitizer does not cause the accelerative degradation of unfilled HDPE film but yields the accelerative degradation of the 20% CaCO_3 filled HDPE film ($A = 3.3$).

The 0.5% 2-methylantraquinone causes the accelerative degradation of 20% CaCO_3 filled HDPE film, ($A = 9.6$). The 0.25% 2-methylantraquinone 20% CaCO_3 filled HDPE film gives the similar result, the accelerating factor is 8.0 which is much higher than unfilled HDPE film ($A = 3.3$).

It is also found that the unsensitized 20% calcium carbonate filled HDPE film has the higher accelerating factor ($A = 3.8$) than unsensitized unfilled HDPE film, ($A = 1$). The benzophenone affects accelerating factor of 20% calcium carbonate filled HDPE film, that rises from 2.0 to 5.3 and 1.7 to 3.6 for 0.5% and 1.0% benzophenone respectively. The unsensitized 50% calcium carbonate filled HDPE film gives the similar result with unsensitized 20% calcium carbonate filled HDPE film.

For 50% calcium carbonate filled HDPE, the accelerating factor decreases with increasing 2-methylantraquinone content, which decreases from 9.6 to 6.9. For benzophenone sensitized samples, the accelerating factor increases with increasing calcium carbonate content. For different content of benzophenone and at the same content of calcium carbonate, the accelerating factor decreases with increasing benzophenone content. Thus, the suitable content of benzophenone is 0.5%.

Table 4.7 Accelerating factors of outdoor exposure when the failure criterion of 50% loss of elongation is reached

Samples	Time period		Accelerating Factor
	(week)	(hour)	
HD/0/0	9.6	1612.8	1.0
HD/20/0	2.5	420.0	3.8
HD/50/0	2.4	403.2	4.0
HD/0/0.25A	2.9	487.2	3.3
HD/20/0.25A	1.2	201.6	8.0
HD/50/0.25A	1.0	168.0	9.6
HD/0/0.5A	1.0	168.0	9.6
HD/20/0.5A	1.0	168.0	9.6
HD/50/0.5A	1.4	235.2	6.9
HD/0/0.5B	4.9	823.2	2.0
HD/20/0.5B	1.8	302.4	5.3
HD/50/0.5B	1.2	201.6	8.0
HD/0/1.0B	5.7	957.6	1.7
HD/20/1.0B	2.7	453.6	3.6
HD/50/1.0B	1.3	218.4	7.4

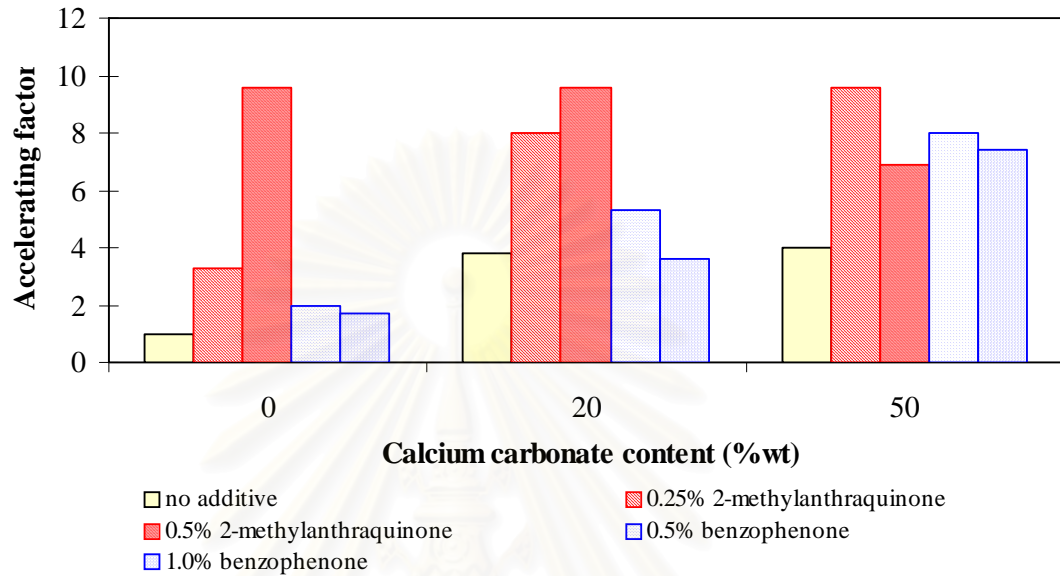


Figure 4.18 Effect of calcium carbonate on accelerating factors of outdoor exposure when the failure criterion of 50% loss of elongation is reached

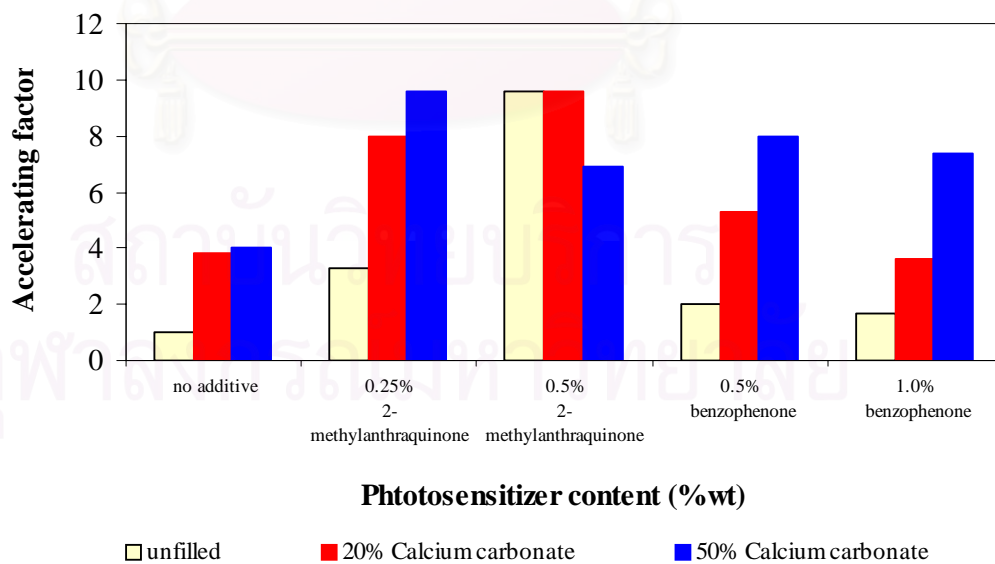


Figure 4.19 Effect of photosensitizers on accelerating factors of outdoor exposure when the failure criterion of 50% loss of elongation is reached

4.4 Proposed Degradation Phenomena

With the presence of calcium carbonate and photosensitizer in HDPE, every sample shows the fast deterioration in tensile properties after outdoor exposure. The result discloses that HDPE can be rendered degradable by addition of

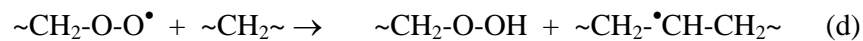
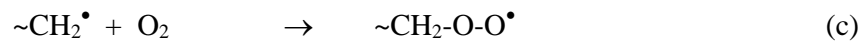
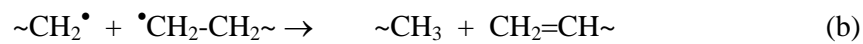
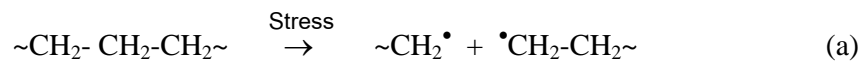
- a) Calcium carbonate particles, which generate macroradicals in PE chain.
- b) Photosensitizer, catalyst for the oxidative degradation of PE chain.

Figure 4.20 shows the possible scheme of degradation of HDPE film. Since calcium carbonate filled HDPE can generate macroradical during processing in extruders by stress induced reaction, the chemical bonds in HDPE chains can be ruptured. Macroradical is generated and can be terminated by oxygen in air, leading to the introduction of carbonyl groups onto HDPE chains. The carbonyl groups initiate degradation or oxidation of the polymer. The experimental results, agree well with the theory, and could be summerized as

1. The tensile properties of unsensitized filled HDPE films decrease with increasing calcium carbonate content.
2. The decrease of molecular weight of unsensitized filled HDPE films (88.3%) is higher than that of the unsensitized unfilled HDPE film (18.3%) after 12- week outdoor exposure.
3. The increase of carbonyl index of 0.25% 2-methylantraquinone sensitized 20% CaCO₃ filled HDPE film is higher than that of 0.25% 2-methylantraquinone sensitized unfilled HDPE film after 12-week outdoor exposure.
4. The unsensitized filled HDPE film exhibits higher accelerating factor than unsensitized unfilled HDPE. The accelerating factor increases with increasing calcium carbonate content.

Figure 4.21 shows the possible scheme of degradation reaction of sensitized HDPE film. The photosensitizers abstract hydrogen or decompose after excitation and cause the initiation of photochemical processes; for example, excited benzophenone can abstract hydrogen from the polymer, or the radical from benzophenone can react with oxygen and form a hydroperoxide radical radical and regenerate a benzophenone molecule. The 2-methylantraquinone exhibits similar behavior. It could be concluded that:

1. The 2-methylantraquinone causes the decrease of the tensile properties more than the benzophenone in HDPE films.
2. The 2-methylantraquinone causes the decrease of molecular weight more than benzophenone in HDPE films after 12-week outdoor exposure.
3. The increase of increasing percentage of carbonyl index of 0.25% 2-methylantraquinone sensitized unfilled HDPE film is higher than that of 1.0% benzophenone sensitized unfilled HDPE film.
4. The increase of accelerating factor of 0.25% 2-methylantraquinone sensitized unfilled HDPE film is higher than that of 1.0% benzophenone sensitized unfilled HDPE film.



in the presence of sunlight

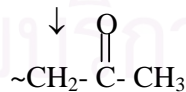
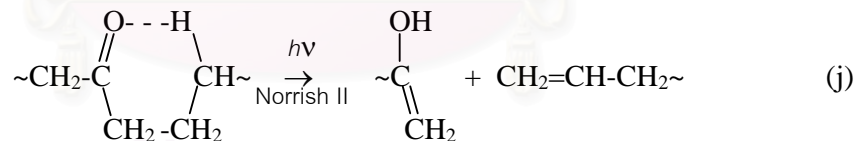
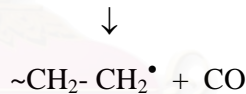
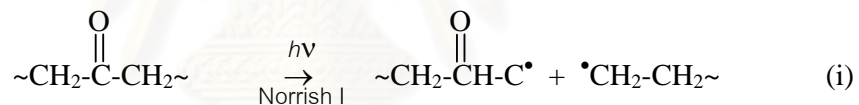
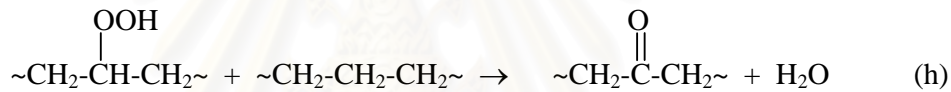
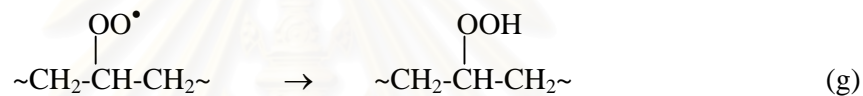
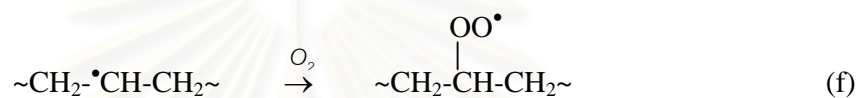
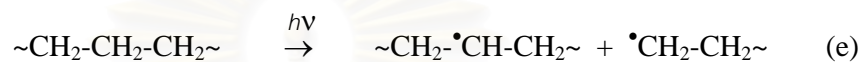


Figure 4.20 Scheme of degradation reaction of HDPE film

For example of 2-methylanthraquinone and benzophenone

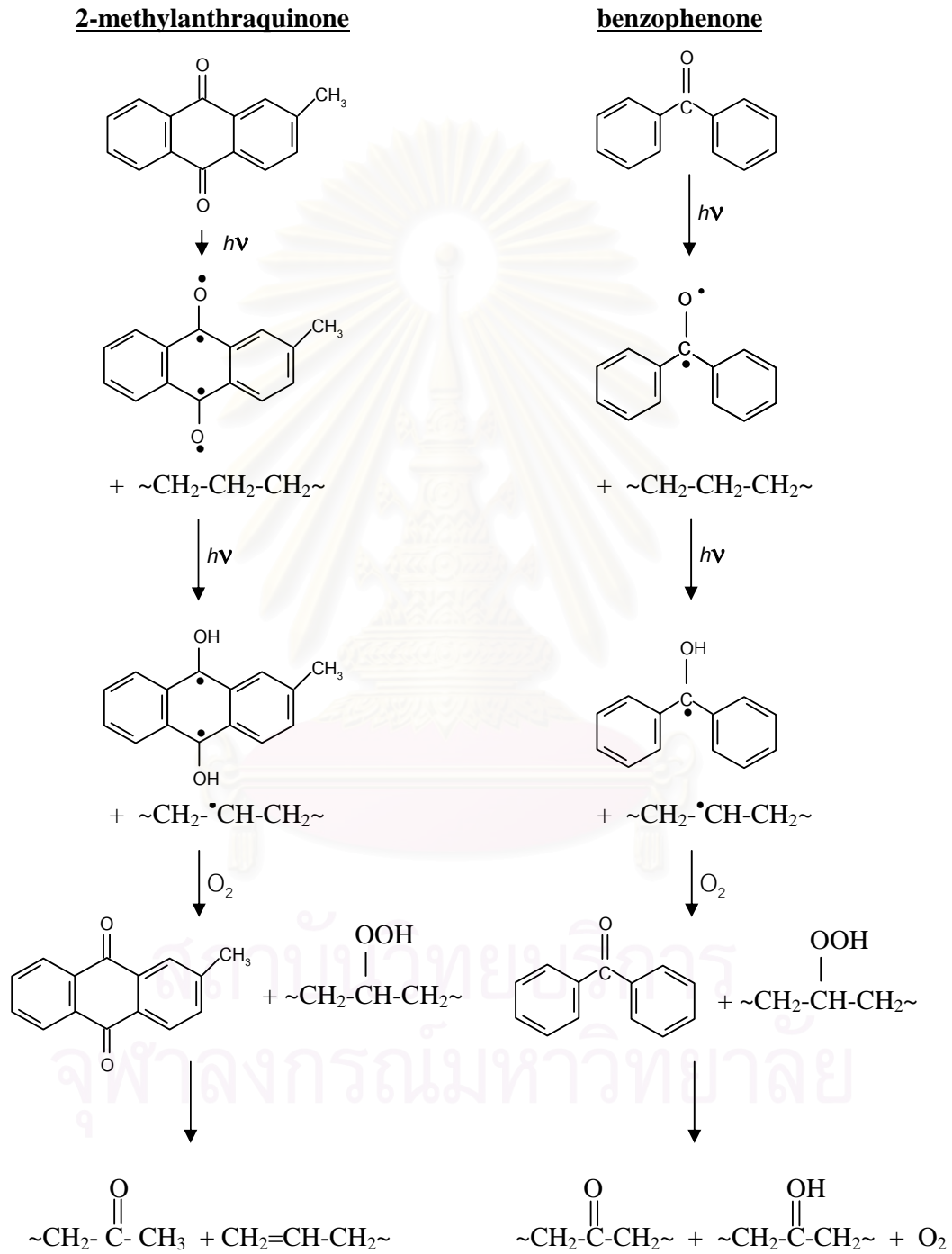


Figure 4.21 Scheme of degradation reaction of sensitized HDPE film

CHAPTER V

CONCLUSION

5.1 Conclusion

Photosensitized calcium carbonate filled HDPE films, were degraded by outdoor exposure. In order to study the behavior of calcium carbonate and photosensitizers in HDPE films and the change of degradation rate, fifteen different formula were used. The CaCO_3 was added in HDPE at concentration of 20 and 50% by weight and two types of photosensitizer, 2-methylanthraquinone and benzophenone were add at 0.25-0.5% and 0.5-1.0% by weight, respectively. All films were exposed outdoor for 12 weeks. The samples were collected and then were stored in the dark until testing. The properties which were observed before and after tests are as follows: tensile strength, elongation at break, molecular weight by viscosity method and fourier transform infrared absorption. The changes in physical and chemical properties of each film were studied. The result are summarized as follows:

Calcium carbonate can play an important role in accelerating the degradation reaction process in plastic as follows:

- a. Calcium carbonate causes the reduction of the plastic tensile properties. The more CaCO_3 content, the less tensile properties.
- b. Calcium carbonate causes the decrease of the molecular weight of HDPE.
- c. Calcium carbonate can enhance the efficiency of photosensitizers to accelerate the degradation reaction. The increase of carbonyl index of 2-methylanthraquinone CaCO_3 filled HDPE is higher than that of benzophenone sensitized CaCO_3 filled HDPE.
- d. The unsensitized filled HDPE films exhibits the higher accelerating factor than unsensitized unfilled HDPE film. The accelerating factor increases with increasing calcium carbonate content.

Photosensitizers can accelerate the degradation reaction. For different photosensitizers, samples sensitized with 2-methyl anthraquinone give the higher degradation rate (tensile properties, molecular weight, carbonyl index and accelerating factor) than films sensitized with benzophenone.

5.2 Suggestion for Future Work

In the area of photosensitized calcium carbonate filled high-density polyethylene films, further study should be done to the following aspects:

1. Photo-degradation of photosensitized calcium carbonate and starch filled high-density polyethylene films.
2. The effect of other photosensitizers or prooxidants on degradation of HDPE film.
3. The plastic should also be relatively inexpensive to be manufactured and still have a product, which is easily blended and have a possibility to be processed in a desired form.
4. The improvements of composite HDPE films cause a better elongation at break.

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Appendices

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APPENDIX B

SAMPLE CALCULATION

Calculation of Intrinsic Viscosity (ASTM D1601)

1. Relative Viscosity (viscosity ratio)

Calculation of the relative viscosity for each concentration is measured from the average efflux time as follows :

$$\eta_r = t / t_0$$

where η_r = relative viscosity (viscosity ratio)
 t = average efflux time of solution
 t_0 = average efflux time of solvent

2. Intrinsic Viscosity (logarithmic viscosity number)

Calculation of the inherent viscosity for each concentration is measured as follows :

$$\eta_{inh} = (\ln \eta_r) / C$$

where η_{inh} = inherent viscosity at concentration C
 $\ln \eta_r$ = natural logarithmic of the relative viscosity
C = concentration on grams/ ml of solution

3. Specific Viscosity

$$\eta_{sp} = \eta_{sp} - 1$$

where η_{sp} = specific viscosity

4. Reduced Viscosity

$$\eta_{red} = \eta_{sp} / C$$

where η_{red} = reduced viscosity

5. Intrinsic Viscosity

In four logarithmic viscosity numbers are plotted versus their respective concentrations on rectilinear graph paper and then the four reduced viscosity numbers are plotted versus their respective concentrations on the same graph. The slopes of these two lines will not be the same, but they converge to the same value at zero concentration. The intrinsic viscosity, $[\eta]$, is the intercept of the line at zero concentration.

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Example B.1 Intrinsic viscosity of original HDPE film

Viscosity measurement of HDPE for original test sample at 135°C

Concentration (g/dl)	t_1	t_2	t_3	t_{avg}	η_r	η_{sp}	η_{sp}/C	$(\ln \eta_r)/C$
solvent	60.66	60.50	60.59	60.58				
0.140	89.37	89.31	89.28	89.32	1.47	0.47	3.39	2.77
0.084	77.09	77.07	77.03	77.06	1.27	0.27	3.24	2.86
0.056	71.60	71.75	71.81	71.72	1.18	0.18	3.28	3.01
0.028	66.94	66.88	66.96	66.93	1.09	0.09	3.14	3.01

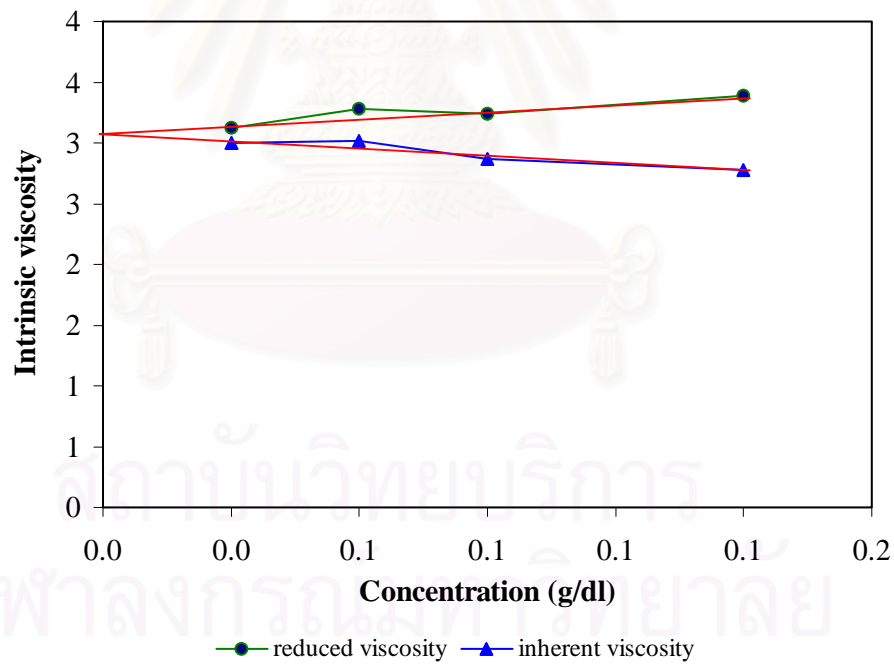


Figure B1 Intrinsic Viscosity of Original HDPE Sample

Intrinsic Viscosity = 3.1

Table B-1 Intrinsic viscosity of photosensitized calcium carbonate filled HDPE film

Sample	Time (week)	Conc. (g/dl)	t_1	t_2	t_3	t_{avg}	η_r	η_{sp}	η_{sp}/C	$\frac{(\ln \eta_r)}{C}$	Time solvent			
											t_1	t_2	t_3	t_{avg}
HD/0/0	0	0.140	89.37	89.31	89.28	89.320	1.474	0.474	3.388	2.773	60.66	60.50	60.59	60.58
		0.084	77.09	77.07	77.03	77.063	1.272	0.272	3.238	2.864	60.66	60.50	60.59	60.58
		0.056	71.60	71.75	71.81	71.720	1.184	0.184	3.283	3.013	60.66	60.50	60.59	60.58
		0.028	66.94	66.88	66.96	66.927	1.088	0.088	3.126	2.997	61.50	61.53	61.59	61.54
	12	0.16680	80.25	80.35	80.25	80.283	1.325	0.325	1.949	1.688	61.50	61.53	61.59	61.54
		0.10008	74.32	74.25	74.35	74.307	1.227	0.227	2.263	2.040	60.66	60.50	60.59	60.58
		0.06672	72.40	72.56	72.44	72.467	1.196	0.196	2.940	2.684	60.66	60.50	60.59	60.58
		0.03336	65.19	65.19	65.19	65.190	1.076	0.076	2.279	2.197	60.66	60.50	60.59	60.58
HD/0/0.25A	0	0.16860	95.62	95.65	95.62	95.630	1.498	0.498	2.953	2.397	63.78	63.81	63.94	63.84
		0.10116	75.41	75.31	75.40	75.373	1.276	0.276	2.725	2.407	59.1	59.13	59.03	59.08
		0.06744	80.90	80.84	80.93	80.890	1.210	0.210	3.114	2.827	66.84	66.84	66.87	66.85
		0.03372	68.28	68.38	68.19	68.283	1.101	0.101	3.005	2.863	62.00	62.00	62.00	62.00
	12	0.1430	66.18	66.12	66.16	66.153	1.097	0.097	0.681	0.650	60.29	60.25	60.31	60.28
		0.0858	64.50	64.53	64.59	64.540	1.051	0.051	0.594	0.579	61.38	61.38	61.47	61.41
		0.0572	63.94	63.90	63.90	63.913	1.040	0.040	0.698	0.684	61.44	61.4	61.54	61.46
		0.0286	61.47	61.43	61.50	61.467	1.020	0.020	0.686	0.680	60.29	60.25	60.31	60.28
HD/0/1.0B	0	0.12640	81.19	81.22	81.28	81.230	1.375	0.375	2.965	2.518	59.1	59.13	59.03	59.08
		0.07584	72.97	72.84	72.78	72.863	1.187	0.187	2.459	2.255	61.38	61.38	61.47	61.41
		0.0556	69.47	69.44	69.37	69.427	1.152	0.152	2.728	2.540	60.29	60.25	60.31	60.28
		0.02528	66.31	66.31	66.40	66.340	1.080	0.080	3.176	3.055	61.38	61.38	61.47	61.41
	12	0.1288	68.81	68.87	68.84	68.840	1.120	0.120	0.932	0.880	61.44	61.4	61.54	61.46
		0.07728	66.22	66.22	66.22	66.220	1.077	0.077	1.002	0.965	61.44	61.4	61.54	61.46
		0.05152	64.40	64.40	64.50	64.433	1.057	0.057	1.109	1.079	60.97	60.97	60.91	60.95
		0.02576	62.28	62.25	62.29	62.273	1.024	0.024	0.947	0.936	60.81	60.81	60.75	60.79

Continued

Sample	Time (week)	Conc. (g/dl)	t ₁	t ₂	t ₃	t _{avg}	η_i	η_{sp}	η_{sp}/C	$\frac{(\ln \eta_r)}{C}$	Time solvent			
											t ₁	t ₂	t ₃	t _{avg}
HD/20/0	0	0.1248	80.78	80.83	80.97	80.860	1.272	0.272	2.180	1.928	63.53	63.53	63.64	63.56
		0.07488	71.53	71.53	71.59	71.550	1.164	0.164	2.192	2.030	61.44	61.4	61.54	61.46
		0.04992	66.41	66.43	66.34	66.393	1.107	0.107	2.135	2.028	60.00	60.00	60.00	60.00
		0.02496	63.10	63.09	63.03	63.073	1.051	0.051	2.052	2.001	60.00	60.00	60.00	60.00
	12	0.1136	66.87	66.94	66.99	66.933	1.103	0.103	0.911	0.867	60.64	60.65	60.68	60.65
		0.06816	67.13	67.16	67.07	67.120	1.019	0.019	0.283	0.280	65.84	65.84	65.87	65.85
		0.04544	65.35	65.43	65.50	65.427	1.050	0.050	1.101	1.074	62.29	62.29	62.35	62.31
		0.02272	64.19	64.22	64.25	64.220	1.008	0.008	0.362	0.360	63.65	63.69	63.75	63.69
HD/20/0.25A	0	0.122	82.97	83.00	83.03	83.000	1.300	0.300	2.459	2.151	63.78	63.81	63.94	63.84
		0.0732	74.47	74.44	74.50	74.470	1.172	0.172	2.343	2.163	63.53	63.53	63.64	63.56
		0.0488	71.10	71.03	71.03	71.053	1.117	0.117	2.407	2.276	63.59	63.6	63.56	63.58
		0.0244	66.82	66.88	66.91	66.870	1.057	0.057	2.352	2.287	63.22	63.18	63.32	63.24
	12	0.132	68.84	68.87	68.89	68.867	1.083	0.083	0.632	0.607	63.53	63.53	63.64	63.56
		0.0792	66.84	66.87	66.97	66.893	1.052	0.052	0.661	0.644	63.53	63.53	63.64	63.56
		0.0528	66.60	66.56	66.63	66.597	1.039	0.039	0.742	0.728	64.14	64.04	64.08	64.08
		0.0264	64.22	64.22	64.19	64.210	1.013	0.013	0.490	0.487	63.35	63.44	63.38	63.39
HD/20/1.0B	0	0.1294	82.87	82.97	83.03	82.957	1.312	0.312	2.409	2.097	63.22	63.18	63.32	63.24
		0.07764	75.91	75.94	76.03	75.960	1.185	0.185	2.386	2.189	64.14	64.04	64.08	64.08
		0.05176	71.13	71.13	71.06	71.107	1.122	0.122	2.352	2.219	63.35	63.44	63.38	63.39
		0.02588	67.63	67.63	67.68	67.647	1.061	0.061	2.343	2.274	63.75	63.78	63.81	63.78
	12	0.1154	67.50	67.44	67.47	67.470	1.088	0.088	0.765	0.733	62.00	62.00	62.00	62.00
		0.06924	65.81	65.81	65.84	65.820	1.053	0.053	0.765	0.745	62.5	62.5	62.53	62.51
		0.04616	65.78	65.81	65.82	65.803	1.033	0.033	0.725	0.713	63.69	63.68	63.65	63.67
		0.02308	64.40	64.41	64.47	64.427	1.008	0.008	0.337	0.335	63.94	63.91	63.94	63.93

APPENDIX C

FTIR DATA

Table C-1 Change in the relative infrared absorbance of samples

Samples	original			12 weeks		
	A_{1715}	A_{1465}	I_{CO}	A_{1715}	A_{1465}	I_{CO}
HD/0/0	0.15572	0.16087	0.96799	0.15984	0.15879	1.00659
HD/20/0	0.16796	0.17308	0.97043	0.16444	0.16804	0.97857
HD/0/0.25A	0.15411	0.15852	0.97215	0.18115	0.16655	1.08763
HD/20/0.25A	0.15608	0.16484	0.94686	0.19783	0.17406	1.13657
HD/0/1.0B	0.16527	0.17164	0.96287	0.15742	0.15706	1.00226
HD/20/1.0B	0.16019	0.17689	0.90557	0.17450	0.17937	0.97285

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APPENDIX D

Time period when the failure criterion of 50% loss of elongation

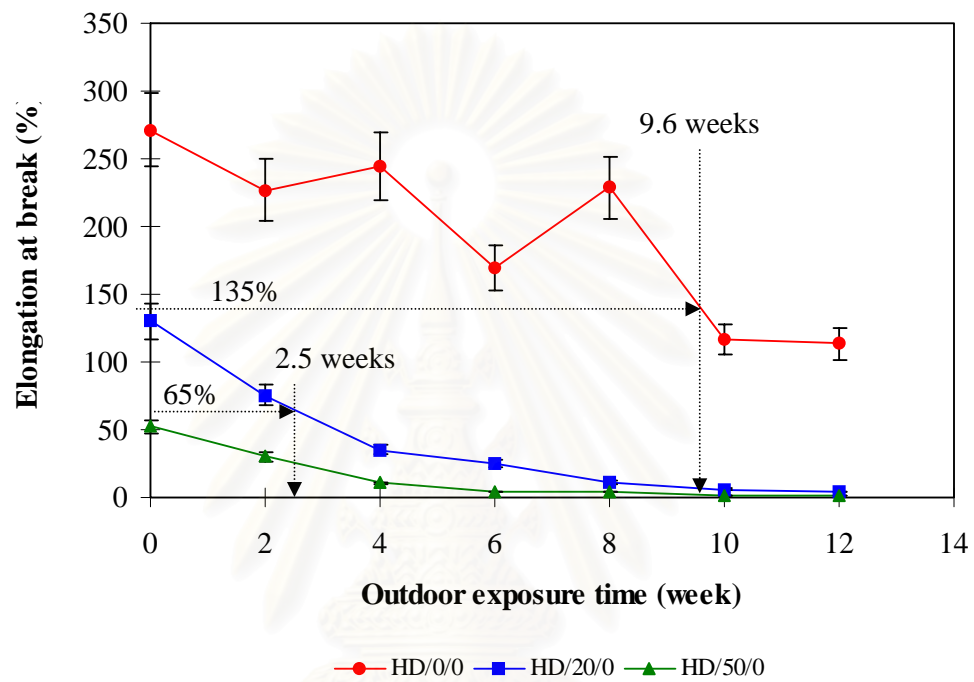


Figure D-1 Time period when the failure criterion of 50% loss of elongation

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