ENVIRONMENTAL ASPECT OF THE POLYSTYRENE FOAM DEGRADATION

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การย่อยสลายของพอลิสไตรีนโฟมในสิ่งแวดล้อม

นายฤกษ์ฤทธิ์ เคนหาราช

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมสิ่งแวดล้อม
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ENVIRONMENTAL ASPECT OF THE POLYSTYRENE FOAM DEGRADATION

Suranaree University of Technology council has approved this submitted in partial fulfillment of the requirements for the Master's Degree

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งานวิจัยนี้ได้ศึกษาการย่อยสลายของพอลิสไตรีนโฟม (PS-Foam) ในสภาวะจำลองสภาวะธรรมชาติ ซึ่งประกอบด้วย สภาวะทิ้งกลางแจ้งให้สัมผัสกับสภาพอากาศธรรมชาติ สภาวะฝังกลบ และสภาวะที่แช่ในน้ำเสียและน้ำทะเล จากการติดตามการเปลี่ยนแปลงค่าน้ำหนักโมเลกุลของ PS-Foam โดยใช้เทคนิค GPC (Gel Permeation Chromatography) ในช่วงระยะเวลา 6 เดือน และได้ตรวจสอบอิทธิพลของ พื้นที่ผิวสัมผัสของโฟม ปริมาณสารอนินทรีย์ไนเตรต และซัลเฟตในดินที่ฝังกลบ รวมถึงปริมาณของสารเร่งการสลายตัว ซึ่งได้แก่ Benzoyl peroxide และ AIBN ที่มีต่ออัตราการย่อยสลายของโฟม

ผลการวิจัยพบว่า เมื่อ PS-Foam ถูกตากให้สัมผัสกับแสงอาทิตย์ในสภาวะทิ้งกลางแจ้ง โฟมเกิดการย่อยสลายอย่างรวดเร็วด้วยปฏิกิริยาการสลายตัวด้วยแสง โดยที่กลไกในการย่อยสลายเกิดจากกระบวนการขาดออกจากกันของโซ่โมเลกุล และระยะเวลาในการย่อยสลายขึ้นอยู่กับค่าน้ำหนักโมเลกุลเริ่มต้นของโฟม ซึ่งพบว่า PS-Foam ใช้ระยะเวลาน้อยกว่า 6 เดือนในการย่อยสลาย และจากการสังเกตเบื้องต้นโดยใช้แบบจำลองทางคณิตศาสตร์สามารถระบุได้ว่าอัตราการย่อยสลายของโฟมมีค่าสูงขึ้นเมื่อเพิ่มปริมาณสารเร่งการย่อยสลาย Benzoyl peroxide บนผิวของโฟม ในสภาวะเร่งโดยการใช้เครื่องเร่งสภาพอากาศ ผลการทดลองบ่งชี้ว่า น้ำหนักโมเลกุลของโฟมที่วัดได้จากเครื่องเร่งสภาพอากาศมีค่าเท่ากับน้ำหนักโมเลกุลที่สังเกตได้จากการทิ้งให้โฟมสัมผัสแสงอาทิตย์และสภาพอากาศตามธรรมชาติ แสดงว่าสามารถนำเครื่องเร่งสภาพอากาศมาใช้ในการศึกษาการย่อยสลายของโฟมได้ และจากการวิเคราะห์ข้อมูลที่ได้จากเครื่องเร่งสภาพอากาศโดยหลักการทางสถิติพบว่า อัตราการย่อยสลายของโฟมเพิ่มขึ้นเมื่อเพิ่มปริมาณสารเร่งการย่อยสลาย Benzoyl peroxide และ AIBN บนผิวของโฟม โดยสารเร่งการย่อยสลาย AIBN สามารถเร่งการย่อยสลายของโฟมได้ดีกว่า Benzoyl peroxide ในการฝังกลบในดินที่มีการเปลี่ยนแปลงปริมาณสารอนินทรีย์ไนเตรตและซัลเฟต ไม่พบการย่อยสลายของโฟมในช่วงระยะเวลาฝังกลบ 6 เดือน จากสภาวะจำลองที่โฟมถูกทิ้งในแหล่งน้ำ ข้อมูลบ่งชี้ว่าโฟมมีอัตราการย่อยสลายที่ช้ามาก และสารผลิตภัณฑ์จากกระบวนการย่อยสลายไม่มีอิทธิพลทำให้คุณภาพของน้ำ (COD) เปลี่ยนแปลง ข้อสรุปสำคัญที่ได้จากการวิจัยครั้งนี้คือ ในสภาวะแวดล้อมธรรมชาติการย่อยสลายของโฟมจะเกิดจากปฏิกิริยาการสลายตัวด้วยแสง

สาขาวิชาวิศวกรรมสิ่งแวดล้อม ลายมือชื่อนักศึกษา..
ปีการศึกษา 2544 ลายมือชื่ออาจารย์ที่ปรึกษา.......................................
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม...................................

REUKRIJ KENHARAJ: ENVIRONMENTAL ASPECT OF THE
POLYSTYRENE FOAM DEGRADATION. THESIS ADVISOR:
ASSIST. PROF. UTAI MEEKUM, Ph.D. 109 PP. ISBN 974-533-030-2

The degradation phenomenon of the PS foam in the conditions imitated to the actual exposure environment, natural light exposure, landfill and water incubated were studied for a period of six months. The effect of photo accelerators, Benzoyl peroxide and AIBN, physical form of the foam sample and the concentration of the inorganic supplementary nutrition, nitrate and sulfate, in the topsoil, on the degradation rate of the PS foam were also included. GPC technique was mainly used to observe the molecular weight reduction.

When the PS foam was exposed under the natural sunlight, it was found that the decomposition by the photoreaction was rapidly occurred. The degradation mechanism of this polymer was chain scission process. The decomposition time was linearly corresponded and depended to the molecular weight of the starting feed stock. The degradation time of this solid waste was less than 6 months. By using the mathematical model, it was preliminary observed that the degradation reaction of the PS foam was increased when the peroxide accelerator was incorporated onto the surface of the sample. In the accelerated condition by using the standard weatherometer chamber, the results were reviewed that the data obtained from the accelerated chamber was identical to those carried out by natural causes and it could be directly applied into the field study. The experimental and statistical calculation results in the chamber were also illustrated that degradation rate of this foam was influenced by the peroxide and AIBN accelerators. The results also indicated that degradation rate was depended on the quantity of accelerator used and the AIBN accelerator had more strongly influence on the degradation rate of PS foam than Benzoyl peroxide. Under the landfill, topsoil having difference in nitrate and sulfate concentration, it was found that molecular weight of the foam could not be decreased within six months buried time. To imitate the degradation of the PS when it was dumped in water resources, the experimental results illustrated that the foam were slowly degraded within six months time and the degraded products did not influenced on the quality, COD, of the incubated water. The main conclusion derived from this work was that photodegradation was the only existing mechanism that the foam could be rapidly degraded.

สาขาวิชาวิศวกรรมสิ่งแวดล้อม ลายมือชื่อนักศึกษา…………………………………………
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Reukrij Kenharaj

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CHAPTER I
INTRODUCTION

1.1 General Introduction

The plastic industry had gained a phenomenal growth during the last decade and become the most widely used material, surpassing even steel. Plastics are currently used in every segment of business and in dailylife. They are found either in the form of entire product such as containers and fast food packaging, or used in the combination with other materials. The later applications include transportation vehicles, computers, tools, recreational equipment, etc. Polystyrene(PS) is the one of the polymeric materials that has contributed a significant part in the plastic production. In 1990, it was produced about 2.44 millions tons per year [Bisio and Xanthos (1995)].

The PS can be categorized into three groups depending on their chemical constituents. They are in the form of single component called general purpose PS (GPPS), polymer blending and/or copolymer, known as High Impact Polystyrene (HIPS) and Acrylonitrile-Butadiene-Styrene copolymer(ABS), and expandable PS (EPS) or PS foam. The PS foam is widely used in food packaging and as insulators. The former application is commonly seen as take-away meal boxes, and disposable chilled containers. When PS foam reach to the end-users, it would be discarded to the environment as municipal solid waste(MSWs). This plastic material is difficult to decompose in the environment. So, the appropriate and well-studied waste management is necessary.

The most well known methods for managing the MSWs are recycling processes, incinerating, landfill and open-air dumping. Each method has definite limitation in respect to economic and engineering point of view. The first one would be the best choice if all of the waste can be recycled and all the consumers have the environmental awareness. Incineration of plastic would generate further hazardous gaseous to the atmosphere if the proper technologies to control the process were not available and well obtained. Landfill seems to be the most acceptable method if a large piece of land is available and is inexpensive. The main disadvantages for the open-air dumping process are that the dumping site would spoil all the near by scenery and it would also transmit infectious diseases. In the past, open-air dumping, landfill and incineration without energy recovery were the main disposal methods. But in the recent years, recycled and well-controlled incineration processes for energy recovery are growing in a high rate. Table 1.1 shows the trend in plastic recycling. The data showed that recycling of all types of plastic are increasing every year.

Table 1.1 Recent Recycling History of Plastics in the U.S

	Plastics Recycled thousand of tons		
	1990	1991	1992
Packaging:			
PET	1,039.0	132.9	182.0
HDPE	62.0	124.7	188.7
PVC	0.9	3.6	4.5
LDPE, LLDPE	19.5	21.3	24.0
PP	-	1.4	6.8
PS	5.9	10.9	14.5
Other	-	-	8.6
Subtotal	200.5	294.8	420.9
Non-Packaging:	27.2	118.8	153.3
Total	**218.6**	**413.6**	**582.8**

[Source: Bisio and Xanthos (1995)]

However, the quantity of the plastic waste that are returned into the recycle and incineration processes has a small fraction when compare to the landfill. Table 1.2 indicates that the approximately 0.22 millions tons and 2.16 millions tons of plastic were recycled and incinerated, respectively. On the other hand, 12.27 millions tons of the waste were disposed in landfill site.

Therefore, the study in degradation of polystyrene foam in the environment would be an interesting issue. The results obtained from this study could be used as the basic information to manage the solid waste derived from the PS foam and other plastic wastes in the future.

Table 1.2 Disposition of Eight Commodity Polymer in 1990 in the U.S

	Thousand of Tons					
	Total Production	Fabrication losses	Addition to inventory	Recycled	Incinerated	Landfilled
LDPE film	2,951.0	29.5	0	8.6	436.7	2,475.7
LDPE non-film	1,945.0	19.5	417.2	0.5	226.3	1,281.6
PVC	3,690.0	36.7	2762.4	2.3	133.3	735.1
HDPE	3,534.0	35.4	459.9	60.8	446.7	2,531.5
Polypropylene(PP)	2,990.0	29.9	532.0	30.4	359.6	2,037.6
Polystyrene(PS)	2,241.0	22.2	275.3	5.9	290.7	1,646.7
Polyurethane(PU)	1,481.0	15.0	709.8	2.7	112.9	640.8
Thermoplastic Polyesters	938.0	9.5	51.2	60.3	115.6	656.7
ABS	460.0	4.5	167.8	1.8	42.6	242.6
Total	**20,230.0**	**202.3**	**5,376.0**	**218.6**	**2164.6**	**12,268.5**

[Source: Bisio and Xanthos (1995)]

1.2 Objectives

In this research study, the degradation of the PS foam in three different disposal environments, landfill, open air dumping, and water dumping were investigated within six months period. The main objectives of the research are;

(i) To study and compare the degradation of the PS foam in the different environment.

(ii) To study the affect of the surface area of the PS foam on the degradation rate.

(iii) To investigate the possibility of using of the accelerators to speed up the degradation rate of the PS foam

(iv) To study the affect of inorganic substrates of the landfill topsoil on the degradation rate of PS foam.

1.3 Scope of Work

Three main disposal sites were used to imitate in this study. They are open air dumping, water dumping and landfill. In order to shorten the degradation time of the sample when subjected in open air dumping, the artificial environment by using the Weatherometer chamber were employed. Benzoyl Peroxide(BPo) and Azobisisobutyronitrile(AIBN) were also used to accelerate the degradation reaction. The wastewater and seawater were used to represent the degradation rate of the plastic when it was disposed into canal and then eventually reached to the seashore. In the landfill study, the surface area of the plastic samples by mean of changing the physical form and also the dependency of the Sulfate and Nitrate concentration of the topsoil were investigated. The number average molecular weight($\overline{M}_n$) characterized by Gel Permeable Chromatography(GPC) were mainly used to monitor the progress of degradation reaction. Chemical Oxygen Demand(COD) was employed to observe to quality of the incubated water.

CHAPTER II
LITERATURE REVIEW

2.1 General Background on Polymer Degradation

Degradation of polymer may occur during the fabrication processes, service life and dispose. There are several factors contributed on the degradation of polymer. The most important ones are thermal degradation, weathering, chemical degradation and environmental stress cracking, ionizing radiation, wear and erosion and biodegradation. Plastics may be exposed to one or several of these factors, depending on the type of plastic processing or the service conditions. The combination of factors such as wear combined with weathering or the present of oxygen and radiation may cause higher degradation rate than only one factor. In the aspect of environmental engineering the thermal degradation, environmental degradation and biodegradation are very important. Thermal degradation was appeared in the recycling process of plastic waste. Environmental degradation and biodegradation was occurred during the service lifetime and disposal. Deterioration of polymer to normal environmental conditions is called weathering or environmental degradation. The factors that are contributed to the environmental degradation include radiation, oxygen, moisture, temperature cycling and atmospheric contamination. In this chapter, a briefly description on thermal degradation, environmental degradation and biodegradation of polymer especially for the PS are described.

2.2 Thermal Degradation of Polymer

The polymer can be easily undergone thermal degradation. It proceeds through free radical mechanism, which is initiated by random chain scission [Carmeron and McCalumm (1967); McNeil, Zulfiqar and Kousar (1990)]. This reaction mechanism is called thermally depolymerization. A number of academic researchers have studied on the kinetics of the thermal decomposition by using thermogravimetric analysis

(TGA) measurements [Westerhout *et al.* (1997)]. Likewise, Madras *et al.* [1997] had recently developed the degradation model to described the molecular weight distribution(***MWD***) evolution during the PS thermal degradation.

It was found that one of the major products obtained from the thermal degradation of the PS plastic is the starting monomer. This process can be found for both low and high temperature degradation. Schröder and Ebert [1984] studied the thermal degradation of PS at temperatures of about 300°C and three types of yielding products were identified. They were primary product, intermediate product and stable final product. The primary products including styrene diphenylbutene, triphenylhaxene and other trimers. They were formed almost instantaneously and their concentration decreases with the degradation time. The intermediate products showed the maximum concentration and then were converted into final stable products at high conversions. The common intermediate compounds were α-methylstyrene, diphenylpropane and diphenylbutane. The concentration of the stable final products, toluene, ethylbenzene, cumene and triphenylbenzene, were increased with the increasing of the reaction time.

Zhang *et al.* [1995] has reported that the thermal degradation of PS in fixed bed reactor at 350°C under the nitrogen flow give rise to the styrene selectivity of 70 wt % with a conversion more than 80 %. Other by-product were the styrene dimer, α-methylstyrene, toluene and ethylbenzene. The changing in by-product, from styrene to ethylbenzene, in thermal degradation of polystyrene at temperature ranging from 360 to 420°C was observed by Carniti *et al.* [1991]. It was found that the styrene/ethylbenzene ratio was decreased with both the reaction time and the reaction temperature. The result is shown in Figure 2.1. It is illustrated that the decreasing in the ratio with both time and temperature suggested that styrene was initially formed, which is then further converted into ethylbenzene.

Williams *et al.* [1993, quoted in Aguado and Serrano, 1999] analyzed the composition of the oils generated during PS degradation at 500°C in a batch reactor with secondary degradation of the volatile products at 500, 600 and 700°C, respectively. The main products obtained from this process were styrene, benzene, xylene, toluene, styrene oligomers, and a number of alkylated styrene derivatives. Moreover, the variety of polyaromatic hydrocarbon(PAHs) were also detected such as phenenthrenes, fluoranthenes, benzopyrenes, chysene, etc. Most of these components have been known as carcinogenic and/or mutagenic agents. The concentration of PAHs increased with the temperature of the secondary cracking.

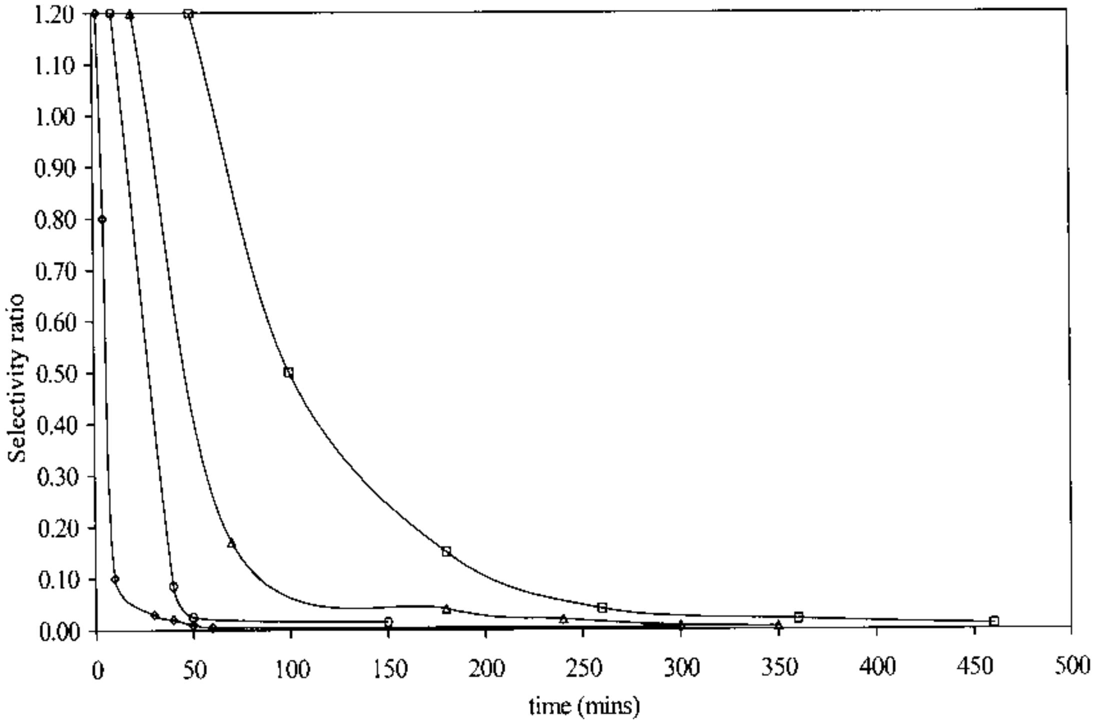


Figure 2.1 Evolution of the styrene/ethylbenzene ratio with the time during PS cracking at different temperatures; (□) 360°C, (Δ) 380°C, (O) 400°C and (◊) 420°C[Source: Carniti *et al.* (1991)]

Murakata *et al.* [1990, 1993] studied the effect of different solvents on the thermal degradation of PS in the temperature ranging from 250 to 450°C. The stirred autoclave reactors were employed. Thermal degradation of polymers in solution can be advantageous because it is not hindered by the mass and heat transfer limitations present thermally treating pure polymers. The presence of solvent had an affect to both the PS conversion and the product distribution. The most pronounced reduction in PS conversion was observed in the presence of tertralin, which is a solvent with a hydrogen donating ability. It was explained by hydrogen abstraction from the solvent to intermediate polymer radicals and resulting in an interruption of the propagation reactions of PS depolymerization. The highest conversions were obtained with the phenolic solvents, because the phenoxy radicals enhanced the degradation of PS in the hydrogen abstraction processes.

Degradation of PS in the presence of solvents was also applied to the conversion of other PS family, such as poly(p-methylstyrene) and poly(p-styrene-allyl alcohol)[Murakata *et al.* (1993); Madras *et al.* (1995)]. Figure 2.2 shows the temperature depend of conversion of poly(p-methylstyrene) when using phenol, 1-methyl-naphthalene and tertralin as solvents. It is indicated that tetralin leads to the greatest degradation below 370°C. These results conclude that the effect of the solvent in the degradation of styrenic polymers is strongly influenced by the temperature.

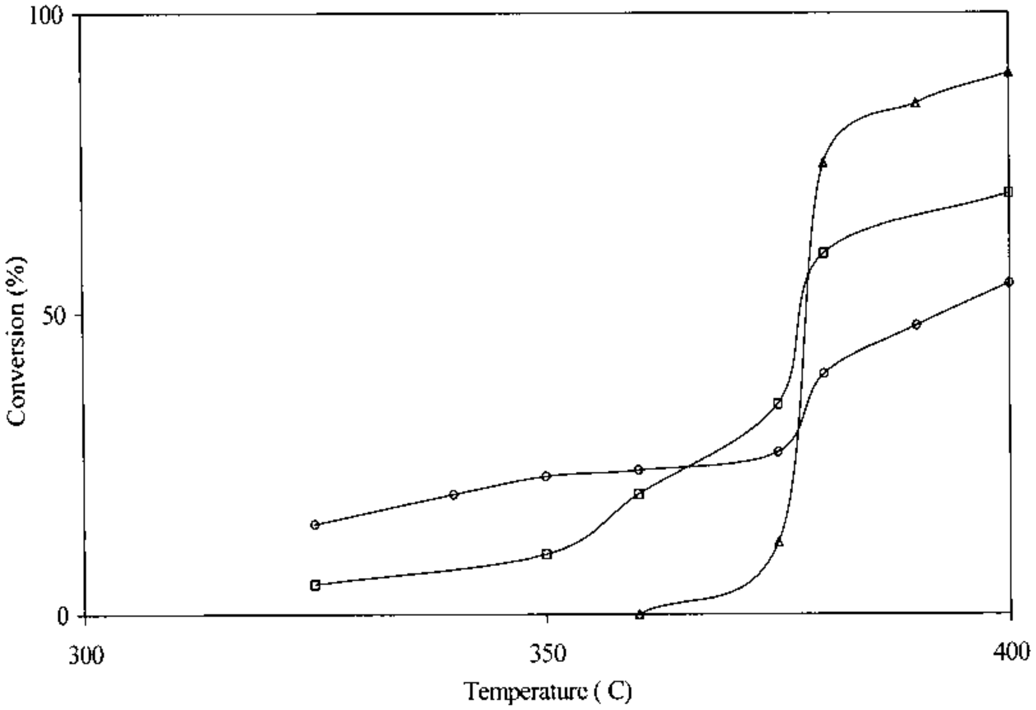


Figure 2.2 Temperature dependence of the poly(p-methylstyrene) conversion in the presence of different solvents: (Δ) phenol, (□) 1-methylnapthalene and (o) tetralin [Source: Murakata *et al.* (1993)]

A new approach to PS thermal degradation was further studied by Beltrame *et al.* [1997] based on PS conversion in the presence of water. The experiments were performed at temperatures between 300 and 350°C in the closed autoclaves under pressure and in argon atmosphere. Styrene was confirmed as the intermediate by-product. It was then further converted into toluene and ethylbenzene. Thus, styrene can be selectively formed with this system only at short reaction times. The presence of water caused an increase in both the yield of light products and the styrene selectivity. Beltrame have concluded that water appears to prevent intramolecular and intermolecular hydrogen transfers and consequently shifts of the radicals along and also between the polymeric fragments.

High yields of the starting monomers were also obtained in the pyrolysis of PS. Erricsson [1985, quoted in Aguado and Serrano, 1999] showed that PS degradation in the commercial pyrolyser leads to styrene yields of over 60%. Increasing in the pyrolysis temperature resulting in the lower of the monomer product. The highest styrene yield, around 80 wt %, was obtained at 600°C. The similar results were obtained by Audisio and Bertini [1992, quoted in Aguado and Serrano, 1999] when study carried out at the temperature between 600 and 750°C. In contrast with the degradation of PS at low temperature, it was found that the significant amounts of benzene were detected in the pyrolysis product. The styrene yields were also correlated with the molecular weight of PS. Longer PS chains led to higher proportions of styrene. They propose that styrene is formed by β-scission reactions whereas toluene, ethylbenzene and α-methylstyrene are formed essentially by intramolecular hydrogen transfer.

The type of reactor are not effected on the selectively to styrene during the PS pyrolysis. Sinn *et al.* [1976, quoted in Aguado and Serrano, 1999] reviewed that styrene yield of 69.8 and 71.6 % can be achieved by the pyrolysis carried out in a sand fluidize bed reactor at 640 and 740°C, respectively. Moreover, Styrene yields of up to 92 % have recently been reported by Lovett *et al.*, [1997]. The reaction was carried out in a micro-reactor at high temperature 960°C and in very short residence time, 500 ms.

2.3 Environmental Degradation of Polymer

Plastic products can be degraded under the exposion to certain natural environmental conditions. Its degradation rate depends on the weather and on the type of polymer. Weather constituents that have significant deteriorating effects on polymers include solar radiation, oxygen, temperature, humidity and atmospheric contamination. The complexity of plastic weathering was related not only to the large number of factors. Some factors may also be combined to create a synergistic effect on the degradation process. The influence of weather factors on the degradation of polymer is being briefly described in this section.

Solar radiation is the one of main principally factors that significantly influence on the degradation of polymers. It is commonly divided into the following classifications, in order of increasing the wavelength; gamma rays and x-rays, ultraviolet, visible light, infrared, microwave, and radio frequency, as shown in Figure 2.3. The shortest wavelength radiation from the sun comprised much of the Ultraviolet(UV) but the atmosphere of earth filtered it out before reaching the earth surface. Figure 2.4 shows the amount of solar UV and visible light falling on earth in an area of moderate climate during summer as function of wavelength. The shortest wavelength in sunlight is about 295 nm. It contained approximately 5 % in the sunlight and reaches to the surface of earth. It is probably responsible for damaging to plastics [Mustafa (1993)]. The energy carried by radiation is inversely proportional to the wavelength. A certain minimum energy must be delivered to a chemical molecule to break the bonds between atoms. Guchter and Muller [1985] stated that a critical threshold wavelength radiation had enough energy to cause a degradation reaction for each type of chemical bond. Light with a shorter wavelength can also break the polymer bond. The intensity of radiation does not influence the process and the light with a wavelength longer than the threshold is not harmful to a molecule. The threshold wavelengths for various bonds existing in polymer molecules is shown in Table 2.1.

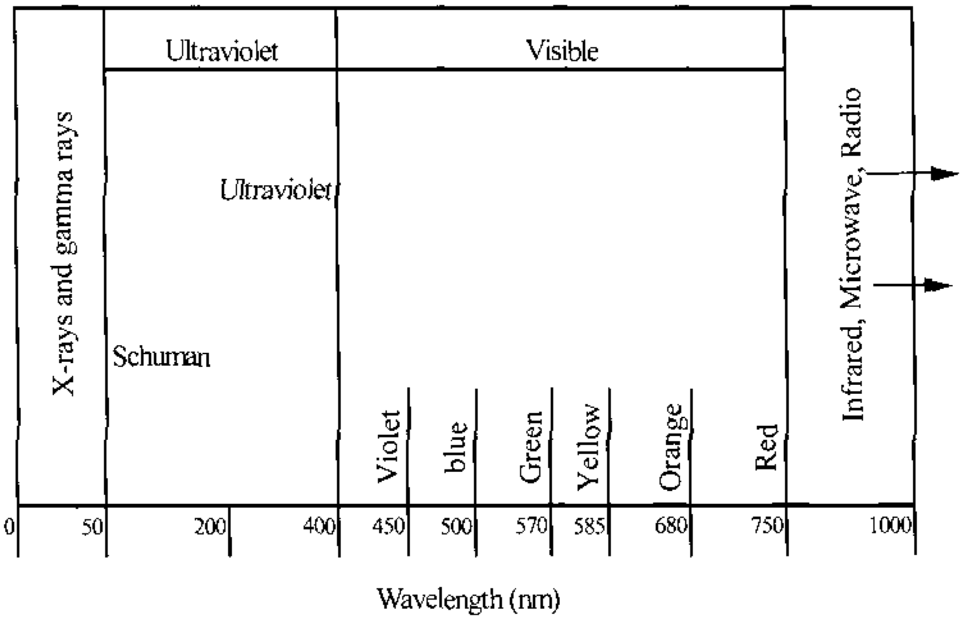


Figure 2.3 Classification of electromagnetic radiation [Source: Mustafa (1993)]

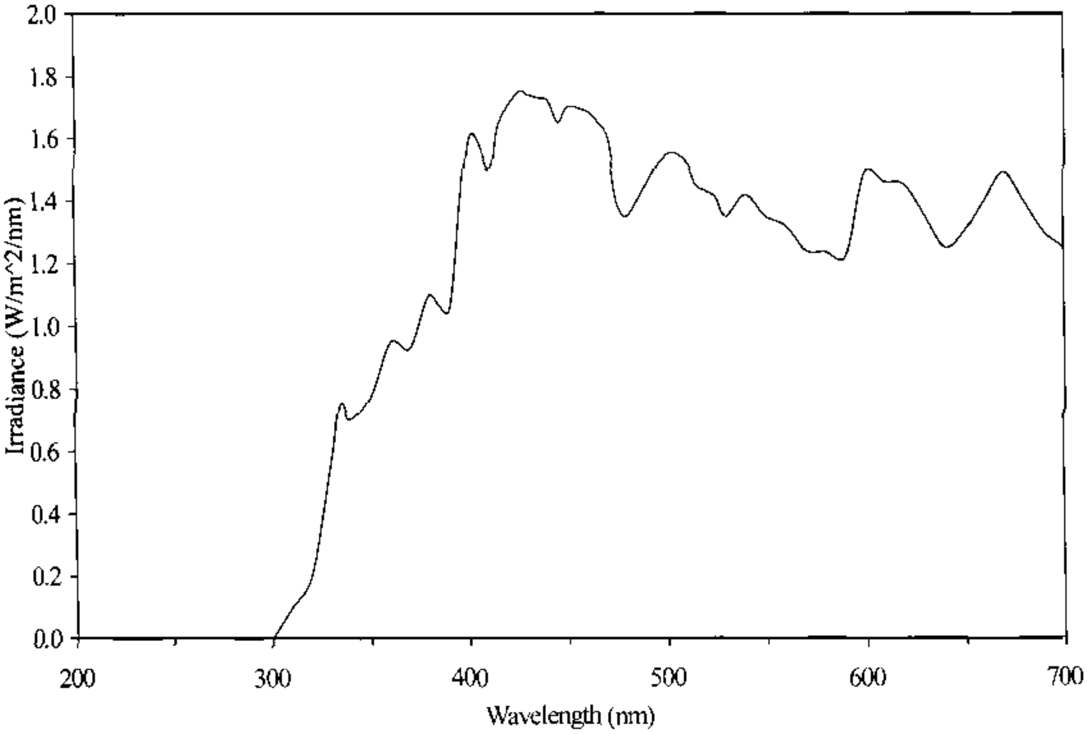


Figure 2.4 Solar ultraviolet and visible radiation reaching the earth during the summer in a area with moderate climate [Source: Mustafa (1993)]

Hivt and Secirle [1964, quoted in Mustafa, 1993] measured of activation spectra, the wavelength corresponding to the maximum damage of polymer, for various polymers by passing the light from an artificial source through a monochromotor to disperse the light into its constituent wavelengths. The spectrum was projected into the test sample and the resulting damage was measured. Activation spectra of some polymers are illustrated in Table 2.2.

Table 2.1 Threshold UV wavelengths for breaking various bonds

Bond	Dissociation energy (kcal/g-mol)	Threshold wavelength below which bond will break (nm)
C-N	72.8	392.7
C-Cl	81.0	353.0
C-C	82.6	346.1
S-H	83.6	344.5
N-H	85.0	336.4
C-O	85.5	334.4
C-H	98.7	289.7

[Source: Guchter and Muller (1985)]

Table 2.2 Activation spectra for various polymers

Polymer	Wavelength of Maximum Damage (nm)
Polycarbonate film	285, 305, 330, 360
Acrylic	290, 325
Styrene-acrylonytrile polymer film	290, 325
Cellulose acetate butyrate film	295, 298
Polyethylene	300
Polypropylene	310, 370
PVC	320
PET	325
PVC-vinyl acetate copolymer	327, 364

[Source: Mustafa, 1993]

The degradation rate of polymers in environment had differed in the different location and also were depended on the time of year, latitude, time of day, altitude above sea level, and local atmospheric conditions. Lee [1991] observed that the photoactivated and nonphotoactivated polyethylene(PE) and several types of plastic bag film samples were degraded significantly when exposed to outdoor weather in a subtropical climate condition. The film had lost 80% of its original elongation after outdoor exposure for 90 days. All film became entirely brittle after exposure for 120 days. But in the study done by Atorngitjawat [1996], it was found that High-density polyethylene(HDPE), Low-density polyethylene(LDPE) and Polypropylene(PP) films became brittle after exposure in the outdoor weather of tropical climate for 36, 161 and 168 days, respectively.

Oxygen is also one of the factors that had influence on the photo aging of polymer. It may absorb the ultraviolet and start a primary photochemical reaction. Radiation, in the presence of oxygen, leads to polymer oxidation. Photo-oxidation is a mechanism that is responsible for most of the damage to plastic by ultraviolet radiation. The reaction was initiated by free radical created by a rupture of C-C main chain bonds or the impurities introduced into the polymer chain during polymerization [McCallum, 1985 quoted in Mustafa, 1993].

Rabek *et al.* [1993, 1996] reviewed that the degradation of PS when exposed to sunlight and to the artificial light was accelerated by photoinitiators such as ketones, quinones and peroxides. They absorb light up to about 380 nm, which cause their excitation or cleavage into free radicals. They may initiate polymer degradation and other transformations by abstraction of hydrogen atom from a chain and formation of polymer alkyl radical. The influence of photoinitiators action depends on the atmosphere, temperature and solvent. According to the studied by Kazcmerek and his coworkers [2000], they found that benzophenone, antraquinone and benzoyl peroxide were accelerated and increased the efficiency of photo-oxidation process of PS. These photoinitiators were inhibited the photocrosslinking and formation of double bonds in the polymer chain. Benzophenone has the greater activity as photoinitiator when compared to antraquinone and benzoyl peroxide.

Halogen compound is one of the additives that is evidently found to accelerate the photodegradation of PS. Torikai and his colleagues [1995] studied the effect of the flame-retardant, containing bromine, on the photodegradation of PS. The results showed that the efficiency of degradation was depended on the irradiation wavelength and also the chemical structure of the additives. In most cases, degradation rate was increased by addition the flame retardant. The halogen atom played a significant role in the degradation of PS by abstract hydrogen from the α-position of styrene repeated unit and resulting the polystyryl radical. Then, the radical acts as the precursor of photodegradation. Consequently, the degradation of the PS is increased. Terikai *et al.* [1998] further studied that the number of bromine atom in the molecule and concentration of bromine molecule in PS compound should affect the efficiency of photodegradation of PS. The most effective wavelength for main chain scission of PS was 280 nm for the sample containing 1 phr of flame retardant, while the wavelength shift to 300 nm for the samples containing 2 phr of the flame retardant. In the studied by Torikai and Hasegawa [1999] on the accelerated photodegradation of poly(vinyl chloride)(PVC) showed that the accelerated photodegradation of PVC under terrestrial sunlight (wavelength longer than 290 nm) was occurred when introducing the abnormal bond into the polymer chain by pre-irradiated the PVC samples with shorter wavelength radiation. The degradation rate of this polymer was depended on both wavelength and the pre-irradiation time.

Temperature had also evidently influenced on the photodestruction of polymer. Winslow [1972, quoted in Mustafa, 1993] pointed out that temperature had influenced on photochemical reactions and given rise to polymer aging in two ways. Firstly, it accelerated the destructive effect of UV exposure. Then, it might reach a range at which thermal oxidation occurred. It was observed that photochemical reaction often follow widely known rules that a 10°C increasing in UV exposure temperature, it would doubles the degradation rate. According to Torikai *et al.* [1986], they found that accelerated degradation rate achieved by increasing the molecular mobility of polymer molecule. It was possibly done by raising the temperature to above the glass transition temperature(T_g). The temperature dependence of oxidation rate of branched polyethylene exposed to a fluorescent lamp was shown in Figure 2.5.

An additional factor that is not frequently taken into consideration, is the effect of low temperature. Plastics exposed to outdoor temperatures below their T_g become brittle. The presence of water in the form of rain or dew is an important, but not always fully recognized, factor in polymers degradation. Even inland materials are wet for relatively long periods. Rain is one factor creating the wetness. The second factor is dew. Dew is the condensation product of moisture in the air and it is formed at relatively low temperature. Dew is saturated with oxygen and may cause damage by bringing oxygen into close contact with the material and thereby promoting oxidation. Water may influence radical activity during plastic photodegradation. It has been shown that peroxy radicals may complex with hydrogen-donating compound and lead to a reduction in radical activity. Further damage to plastic can be created when water frozen in the fine cracks of material. It is then promoting the creation of internal stress.

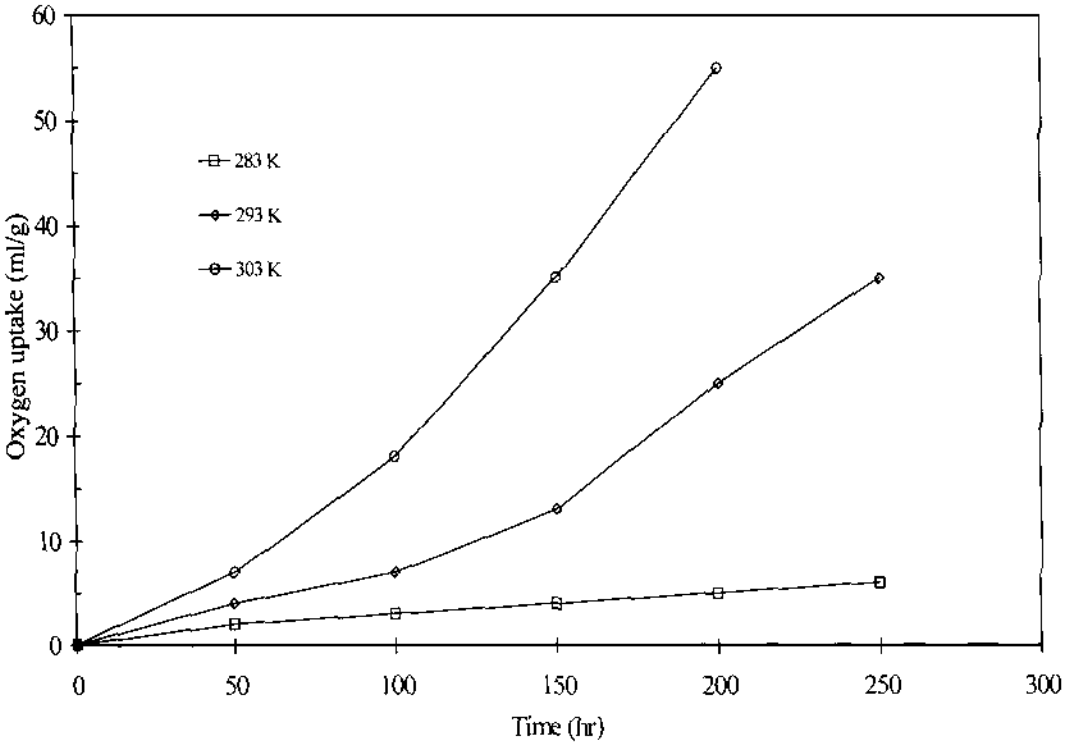


Figure 2.5 Oxidation rate of polyethylene exposed to UV radiation as a function of temperature [Source: Mustafa, 1993]

Atmospheric contamination may be in the form of gases or particles. The presence of dust generally reduces the intensity of solar radiation. However, an excess of sharp particles carried by wind may lead to deterioration of the plastic surface. Industrial air pollution such as Nitrogen Dioxide, Sulfur Dioxide, or Ozone influences the degradation of polymer properties. The additional presence of ultraviolet light and, sometimes, oxygen may further affect polymer deterioration in the presence of pollution. An investigation into the changes in the various properties of polymers exposed to Sulfur Dioxide or Nitrogen Dioxide indicated that viscosity and the percentage of crosslinking may be affected [Jellinek *et al.* (1983)].

The polymer filled with starch and also polymer blends have been found to be more easily degraded by photo acceleration than pure polymer. In the studied by Saleh and Elizabeth [1994] on the environmental degradation of high-density polyethylene(HDPE) blended with carbon monoxide and nonblended HDPE. The results shown that the presence of carbon monoxide in the blend samples accelerates the process of environmental degradation, but the degradation mechanisms appear to be similar to most found in the nonblended HDPE. Kaczmerak [1995] published the results of his studied. The data showed that the polystyrene blended with poly(vinyl acetate)(PVAc) and then was exposed to highly energetic, polychromatic light (248-578 nm). The degradation rate was higher than found in the pure PS. They concluded that the PVAc and its copolymers were more easily photodegraded than PS. This is because of the relatively weak bonds in ester groups, which is approximately 348-390 kJ/mole. In the study by Kiatkamjornwong and co-workers [1999] found that the PS fill with grafted cassava starch was rapidly deteriorated upon the outdoor exposure or UV irradiation. The plastic contained the grafted copolymer required less activation energy to initiate the decomposition process than pure PS.

2.4 Biodegradation of Polymer

Biodegradation refers to the degradation and assimilation of organic polymers and compounds by living organisms, principally microorganism such as fungi, bacteria and actinomycetes. The term can be enlarged to include assimilation by insects, rodents and other animal including man. However, a better term that includes attack by all forms of living thing is biodeterioration. The biodegradation of polymer is the interest issue in the field of polymer and environmental engineering. There are numerous reviews on the biodegradation of both natural and synthetic polymers.

Several researchers studied the degradation of styrene monomer by the microorganisms. The first attempt to isolate styrene-degrading microorganisms from more than 100 soil samples was unsuccessful [Omori *et al.*, (1975)]. Subsequently, Sielicki and coworkers [1978] were studied the microbial transformations of styrene and ^{14}C-labeled styrene in the soil and in the enrichment cultures. They concluded that two different mechanisms were responsible for the disappearance of styrene in the enrichment cultures. In the first mechanism, a mixed population of microorganisms, capable of utilizing styrene as a sole carbon source, oxidized this substrate to phenylethalnal and phenylacetic acid. The later, the culture also mediated polymerization of the monomer to low molecular weight styrene oligomers. This chemical reaction probably occurred as the result of microbial degradation of buthylcatehol, antioxidant polymerization inhibitor present in commercial styrene. In the soil incubation studied, $^{14}CO_2$ evolution from applied ^{14}C-styrene was used to estimate microbial degradation. Approximately 90 % of labeled carbon was evolved from a 0.2 % addition, and about 75 % was lost from the 0.5 % application over 16 weeks period.

Most studies on microbial styrene degradation have focused on anaerobic bacteria, mainly on *Pseudomonas sp.* [Omari *et al.* (1974 1975); Shirai and Hisatsuka (1979); Baggi *et al.* (1983); Higashimaru *et al.*(1983); Utkin *et al.* (1991); O'Connor *et al.* (1995)] and *Clostridium sp.* and *Enterobacter sp.* [Grbic-Galic *et al.* (1990)]. The degradation ability of *Pseudomonas sp.* was due to a plasmid [Ruzzi and Zennaro (1989)]. Other group of researchers studied the aerobic styrene-degrading bacteria isolates belong, for example, to such general as *Alcaligenes* [Tsuchii *et al.* (1977)], *Corynebacterium* [Itoh *et al.* (1996)], *Mycobacterium* [Burback and Perry (1993)], *Nocardia* [Ottengraf *et al.* (1986)], *Rhodococcus* [Warrhurst *et al.* (1994)] and *Xanthobacter* [Hartmans *et al.* (1989)]. The fungi, black yeast *Exophiala jeanselmei*

[Cox et al. (1993)] and some white-rot fungi *Bjerkanderaadusta, Trametes versicolor, Phaneochaete chrysosporium* and *Pleurotus ostreatus*, were also reported to be able to degrade styrene monomer [Braun-Lüllemann *et al.* (1997)].

In the recent years, the biodegradation of polystyrenes and its copolymer had been investigated. Otake *et al.* [1995] observed the degradation of PS in landfill site in which the age of the site was over 30 years. It was found that no evidence of biodegradation observed for the PS degradation. Kiatkamjornwong and co-workers [1999] studied the biodegradation of PS grafted with cassava starch in soil and in Bacteria, *Bacillus coagulants* 352. It was found that starch in composite PS sheets were destroyed by the microorganism. It was indicated that bacteria could promote the biodegradation of PS plastics before other disintegration processes taking place.

It was also evidenced that the present of pyridinum groups in polymer chain enhances its biodegradability. Peng and Shen [1999] pointed out that incorporation of pyridinium group into PS enhanced the biodegradability. The result from GPC showed that the low molecular weight fraction was more easily degraded than the high molecular weight fraction. The study was also reviewed that the molecular weight was decreasing rapidly when the content of pyridinium group in molecular chain was increased.

From the literature review, it is strongly believed that there is no investigation to determine the degradation of PS foam in the general environment such as landfill, in water resources and in the open-air dumping. Therefore, the study in the degradation of the PS foam in these natural environments is an interesting issue in the field of environmental engineering. This research work is aimed to study the degradation of the PS foam in the natural environment. The result data from this study could be used as the fundamental information for proper managing the PS foam and another plastic waste in the future.

CHAPTER III
EXPERIMENTAL METHODOLOGY

3.1 General Background

There were four main research topics in this work. They were degradation by natural exposure condition, artificial accelerated condition, landfill and water incubation, respectively. The experimental procedure was established to imitate the degradation processes of the PS foam in the actual environmental conditions. In order to obtain the progress of the degradation process, the molecular mass by mean of the number average molecular weight($\overline{M}_n$), of the degraded product were determined by Gel Permeable Chromatography(GPC). The absolute molecular weight value by mean of viscosity average molecular weight($\overline{M}_v$) was reconfirmed by dilution capillary viscometry technique. The quality of the incubated water by mean of Chemical Oxygen Demand(COD) was determined. The details of the experimental procedures are described as follows.

3.2 Samples and Chemical Reagents

The main materials used in this study can be classified into 2 categories: (*i*) the PS foam sample and the accelerators to enhance the degradation of the foam, and (*ii*) chemicals used in the molecular weight characterization process.

The PS foam used in this experiment was obtained directly from the unused commercial foam lunch box. It has the initial number average molecular weight, characterized by GPC, of 132,000 g/mol and the molecular weight distribution of approximately 1.90. It was directly used without further treatment. Three typical forms of samples were used in this study. The rectangular shaped specimens with the approximate dimension of 10 cm x 15 cm were manually cut. In order to increase the surface area of the foam by reduction of the specimen size, the coarse and fine crushed samples, with average size of 4 cm^2 and 0.25 cm^2 respectively, were obtained by using the sharped-knife crushing machine. The Benzoyl Peroxide pellet and AIBN powder (Mark Schuchardt^{TM}) were used as accelerators. They were used as received.

Potassium Sulfate and Sodium Nitrate was used as anaerobic bacterial nutrition in topsoil. They were supplied by Carlo Erba^{TM} and directly used without any further purification. The HPLC grade Tetrahydrofuran(THF) supplied by J.T. Beker^{TM} was used as mobile phase for the GPC. It was clarified by membrane filtration and degassing prior to use.

3.3 Experimental Procedures

3.3.1 Natural Exposure Condition

In order to study the degradation rate of PS foam in open-air dumping, the experiment was carried out under tropical climate at the open site of Suranaree University of Technology. The rectangular PS foam sample sheets were used.

The samples were exposed to natural weather by attachment on the standard exposure rack according to the ASTM D 1435-85 (Standard Practice for Outdoor Weathering Plastic), as shown in Figure 3.1. The racks were constructed in angle of 45° to the vertical and its plane was set to direct to the south. From this construction, the samples were exposed to the sunlight for all day long. Only one side of samples was directly exposed to the sunlight. The specimens were allowed to expose to the natural weather condition for a period of 180 days started from August 1999 to March 2000. The test specimen was randomly sampled in every week by using sharped-knife. Its number average molecular weight and molecular weight distribution were, then, analyzed by GPC.

To study the affect of the accelerated agent on the degradation rate of the PS foam, Benzoyl Peroxide was employed. The 1 % by weight of Benzoyl Peroxide

(BPo) solution were prepared by dissolving in styrene monomer. The solution were throughoutly and quickly spread on the surface of the foam by solution brushing. Care must be taken because the solution would dissolved the PS sample. The Benzoyl Peroxide coated sheets were allowed to dry at room temperature for hours. Consequently, the samples were transferred to attach to the standard sample rack as described earlier. The Benzoyl Peroxide coated samples were randomly collected and analyzed for its number average molecular weight and molecular weight distribution every week.

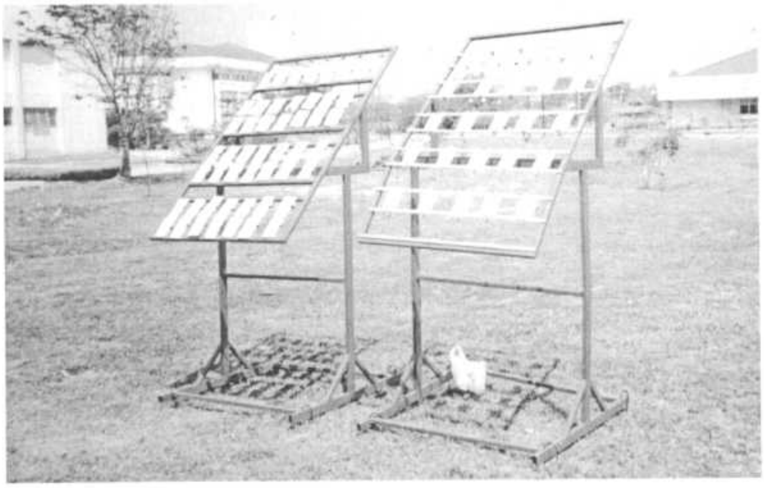


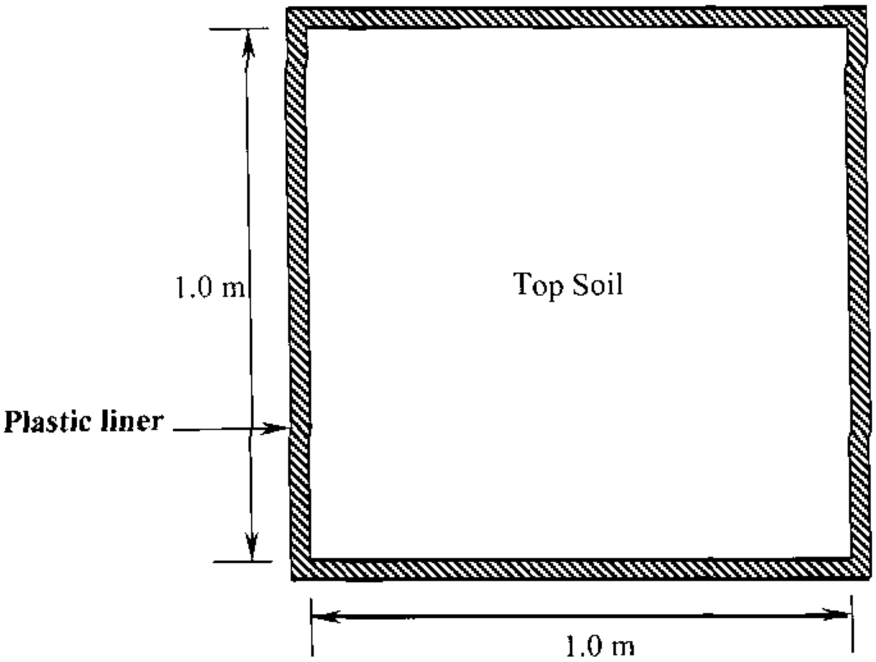
Figure 3.1 The standard exposure rack for natural exposure experiment.

3.3.2 Accelerated Condition

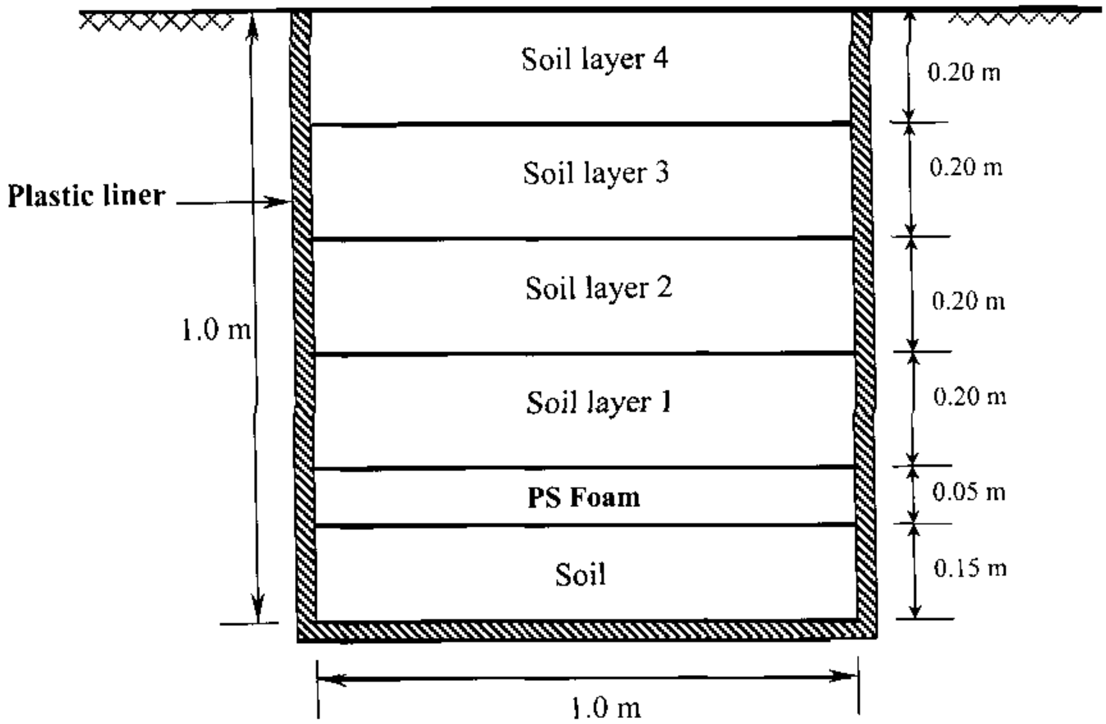
Normally, it would take months to decompose the plastic sample in an open-air dumping. By using the accelerated chamber, the decomposition time would be shortening into weekly time. In order to shorten the degradation time of the PS foam, Standard Weatherometer, S3000 Weatherometer, manufactured by Atlas Electric Devices Co. was used. The detail of this chamber will be given in more detail later on. The exactly the same untreated PS foam sample as describe in 3.2.1 were also employed in this experiment. Two types of accelerating agents, Benzoyl Peroxide and AIBN, were investigated. 1, 2 and 3 % by weight of Benzoyl Peroxide and AIBN solution were prepared by dissolving the exactly weighed of the reagent in 100.00 ml of ethyl alcohol in volumetric flask. The solutions were applied on the surface of sample by thoroughly spraying. The accelerator coated sample sheets were allowed to completely dry by using warmed air drier. Six pieces of each specimen prepared as described above were attached to the standard specimen holder and finally transferred onto circular sample rack holder (see Figure 3.3), which was rotated at 1 rpm. The detail of the test conditions will be fully described in 3.4.3. The samples were turned inside out in every 120 hours of testing cycle. The specimens were also sampled in every 120 hours by using hole puncher with the diameter of approximately 0.5 cm. The number average molecular weights of the sample were resolved by the GPC analysis.

3.3.3 Landfill Condition

In order to study the decomposition of the foam sample by landfill process, the landfill site was constructed at Suranaree University of Technology. The individual landfill cell with dimension 1.0 x 1.0 x 1.0 m^3 were constructed and lined with plastic film as shown in Figure 3.2. The bottom of the cell was overlaid with the excavated soil at the thickness of approximately 15 cm. The crushed foam samples were then regularly spread over. The sample was covered with the multi-layers of topsoil, which was sprayed with anaerobic bacterial nutrition, inorganic Sulfate or Nitrate aqueous solution. Approximately four layers of 20 cm. of the topsoil were used to fill-up the cell. There were two sets of experiments, depend on the physical form of sample, conducted in this study. The high and low surface area samples were investigated. These two types of sample were achieved by using coarse and fine crushed foam sample, respectively. In each set of experiment, the concentration of inorganic Sulfate and Nitrate solution for spraying on the topsoil was varied from 200, 300 and 500 ppm, respectively. The sample was buried for 180 days started from October 1999 till March 2000. The test specimens were collected in every 30 days by using the hollowed metal pipe. The foam samples were cleaned by washing with distilled water and dried at 30 °C in the oven for 24 hours. The samples had been stored in the dark bottle and kept in the refrigerator before analyzing by the GPC technique.



TOP VIEW



SIDE VIEW

Figure 3.2 The landfill cell in landfill condition experiment

3.3.4 Water incubated Condition

It is the fact that some of the solid wastes derived from the PS foam are disposed in to water resources either by human or nature causes including wind. All of the rivers would be polluted by this waste and further harmful to living species in the water. Not only the canals and rivers are contaminated with this plastic. Also, the seashore or even the ocean will be affected from the waste because the barely degraded foam would eventually reach to the area. It would be merit to study the disintegration rate of the PS form in wet environment.

To investigate the degradation of the PS foam in the waters, two water resources, wastewater and seawater were employed to duplicate the deterioration environmental conditions. The swine wastewater from Suranaree University of Technology farm and seawater from the Gulf of Thailand were used. To study the affect of surface area on the decomposition time of the PS foam in the waters, coarse and fine crushed specimen were used. Approximately 5.0 g of the foam sample had been soaked in 2.5 litre of the screw top jar that contained the soaking waters.

There were two sets of experiments for each of the soaking water, depending on the oxygen limitation condition, were conducted in this study. The first one, hereby called "closed system", the container was tightly closed with the screw cap. The outside oxygen would not allowed to distribute into the container during the incubation period. The later set of experiment, hereby called "opened system", the jar was opened to freely expose to the atmosphere. The incubation period used for investigation in this experiment was lasted from October 1999 to March 2000 for 180 days. The foam sample was randomly collected in every 21 days. In order to evaluate the molecular mass of the sample by GPC technique, the solution of the test specimen was clarified membrane filtration.

If the plastic sample degrade during the soaking time, the soaked water would be contaminated with the degraded product. In order to resolve this hypothesis, the effect qualities of soaked water by mean of the COD were performed. Approximately of 30 ml of the soaked water in each experiment was sampled as the same interval as for the sample foam. The COD measurements of soak water were performed according to the standard method of APHA, AWWA and WEF [APHA, AWWA and WEF (1992)]. After the water samples were collected, the total volume of the soaked water was constantly kept by topping it up with the distilled water.

3.4 Instrumentations

The molecular weight by mean of the number average molecular weight($\overline{M}_n$) was mainly used to monitor the degradation rate of the sample in this study. Gel Permeable Chromatography(GPC) was employed. The relative values obtained from the chromatographic technique were reconfirmed by the absolute value derived from the capillary dilution viscometry analysis. In order to accelerate the outdoor weathering condition, The standard weatherometer was employed in this experiment. The detail descriptions of these techniques are being explained in the following section.

3.4.1 Gel Permeable Chromatography

The number average molecular weight and molecular weight distributions of the PS foam sample used in this research work were obtained by the Gel Permeable Chromatography(GPC) technique. The GPC system from Waters^{TM} was employed in this work. Its consisted of a Waters W510 pump, an injector port with 50 μl sample loop, 2 column of Styral gel^{TM} which the molecular weight cut off ranging from 500 to 4,000,000 g/mol, the electrical controlled column oven and the differential reflective index (RI) detector. Data were collected and analyzed on personal computer by using Millennium^{TM} software which was developed by Waters co. Ltd.. THF was used as eluent at a flow rate of 1.0 ml/min. Prior to used, it was clarified by filtration through a 0.45 μm PTFE membrane and then degassed in the sonication bath for 15 minutes. Typically, the test was conducted at the column temperature of 45°C.

Typically, 0.5 % w/v sample solutions in THF were prepared and clarified by micro filtration using 0.45 μm PTFE membrane prior to inject onto the columns. The narrowed molecular weight polystyrene standards supplied by Shodex Standard^{TM} with molecular weights and the molecular weight distribution(***MWD***) as shown in Table 3.1 were used for construction the standard calibration curve.

Table 3.1 The molecular weight and molecular weight distribution of the polystyrene standards

Molecular Weight (g/mol)			*MWD*
$\overline{M}n$	$\overline{M}w$	$\overline{M}p$	
1,215	1,309	1,296	1.08
2,827	2,936	2,959	1.04
9,494	9,658	9,680	1.02
27,833	28,422	28,551	1.03
63,034	64,727	65,931	1.03
166,644	168,862	172,101	1.02
614,823	630,556	629,440	1.03
984,949	1,024,377	995,598	1.04
1,901,389	2,018,877	1,962,687	1.06
3,634,273	3,794,078	3,898,399	1.05

3.4.2 Dilution Viscometer

To determine the absolute value of the viscosity average molecular weight ($\overline{M}_v$) of the sample, the intrinsic viscosity, [η], of the PS sample was determined. The Viscosystem, AVS 360 from Schott Gerate Co. Ltd., was employed. The ubbeholde viscometer capillary types with the total measuring volume of approximately 20 ml were used. The operating temperature used in this work was 34.0±1 °C. Commonly, the initial concentration of 1.00 % w/v sample solutions in toluene were prepared in the 10.00 ml volumetric flask. The solution was then transferred into the capillary and equilibrated for at least 5 minutes. The flow time was measured at least three times by using the online photo switch stopped and the mean average value was obtained. The concentrations the solution sample were proportionally reduced to 0.83%, 0.67% and 0.50%, respectively. They were performed by dilution with 2.00, 5.00 and 10.00 ml of fresh toluene, respectively. The viscosity average molecular weight($\overline{M}_v$) were calculated by Mark and Houwink equation as show follow.

$$[\eta] = K\overline{M}_v^{\,a} \tag{3.1}$$

Where, ***K*** and ***a*** are constants and for the system used in this study, toluene as solvent and measurement of temperature of 34 °C, are 0.0097 ml/g and 0.733, respectively [Brandrup *et al.* (1999)].

3.4.3 Standard Weatherometer

The degradation time of the foam sample were accelerated in artificial environmental condition by using the Standard Weatherometer. The S3000 Standard Weatherometer from Atlas Electric Devices Co. were employed in this study. The equipment mainly consisted of a boro-borosilicate inner filter, the xenon arc lamp, compresses air system and deionized water for using as spraying water. The boro-borosilicate inner filter and the xenon arc lamp were used to generate the continuous UV light at 340 nm. In this study, the power of lamp irradiation was constantly set at 0.50 w/m^2, which is equivalent to the UV energy dose on the sample surface of 1.8 kJ/ (m^2-hr). The compressed air and deionized water were mainly used to simulate the *humidity by mean of rain shower and control the test chamber temperature. During* the experiment, the boro-borosilicate inner filter was replace with a new one in every 600 hours. The back panel temperature was calibrated by using the standard resistivity thermocouple device(RTD) supplied from the manufacture .

According to the weathering data of Nakhron Ratchasima Province obtained by the Climatology Division, Meteorological Department of Thailand as shown in Table 3.2. The data show that the average temperature, relative humidity and rainfall, and total solar radiation in this area were 27.3°C, 68.1% and 85 mm. and 5058.0 MJ/m^2, respectively. The artificial test conditions of the Standard Weatherometer were summarized in Table 3.3. *The parameters were set as similarly as shown in* Table3.2 except the testing temperature. The lowest temperature for the equipment is *65°C. Therefore, testing temperature at 27.3°C that is equivalent to the average value* obtained in the Nakhron Ratchasima region was unable to establish. The irradiation intensity of the Xenon lamp set at 0.50 W/m^2 when exposed to the surface of the samples for 1440 hours was equivalent to the total solar radiation of 5058 MJ/m^2 per year obtained by the sunlight in this region. The mathematical calculation is shown in Appendix A.

Table 3.2 Meteorological data of Maung district Nakhon Ratchasima Province

Meteorological data	Average value(per year)
Temperature(°C)[a]	*27.3*
Relative Humidity (%)[a]	68.1
Rainfall (mm)[a]	*85.0*
Total solar radiation (MJ/m^2)[b]	5058.0

[a] Data collected from January 1987 to 1998 by Nakhon Ratchasima Climate station

[b] Data collected from January 1996 to 1998 by Khonkan Climate station

[Source: Nakhon Ratchasima and Khonkan Climate station, Climatological Division, Meteorological Department]

Table 3.3 The test parameters used for Standard Weatherometer equipment

Condition	Set-up Value
Temperature (°C)	65±4
Spraying cycle (per hour)	Every 2 min.
Irradiation (W/m^2)	*0.50*
Relative humidity (%)	68

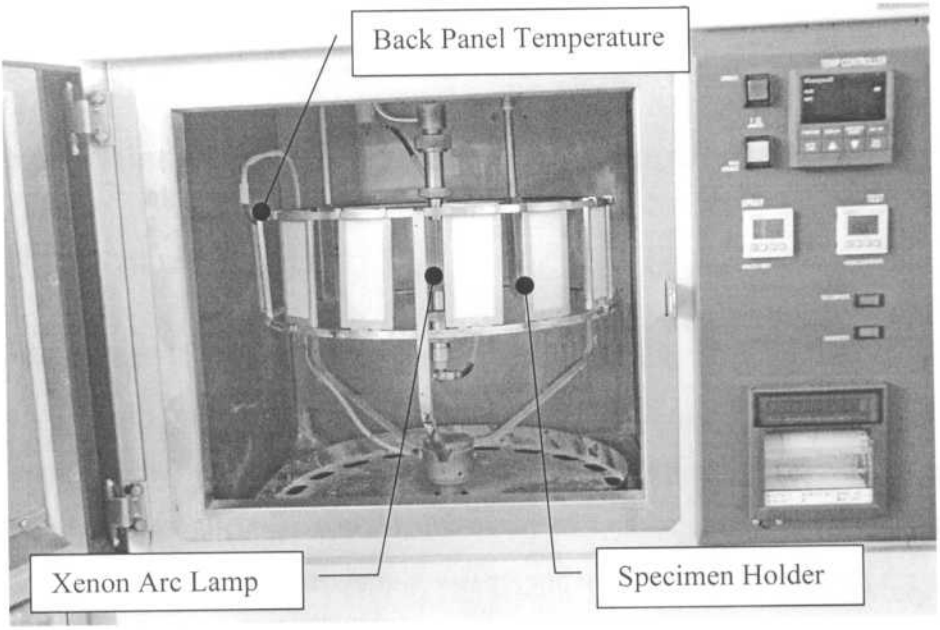


Figure 3.3 The test chamber of Standard Weatherometer

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Degradation of Polystyrene Foam in Open Air Dumping

4.1.1 Natural Exposure

When the PS foam is dumped in the open air, it is mostly degraded by photoreaction. In order to determine the disintegration time of the foam, the experiment was designed for a period of 6 months. The result shown in Figure 4.1 illustrates that the molecular weight, by mean of number average molecular weight ($\overline{M}_n$) obtained by GPC, of the sample was exponentially decreased with the exposure time. The result also indicates two steps of molecular weight reduction. In the first 45 days the molecular was dramatically decreased from 132,000 g/mol to approximately 60,000 g/mol. Then it was almost unchanged for a period of 80 days. After that its molecular weight was again began started to decrease to 20,000 g/mol. At this molecular weight, pieces of specimen were collapsed and felt apart. From this result, it could be suggested that the degradation time of PS foam in the sunlight is around 6 months. By considering the changes in the molecular distribution(***MWD***) of the sample, the plot also shows that there was no significantly increase in ***MWD*** at the first step of deterioration. From the data obtained, it could be pronounced that the initial degradation mechanism of all PS chain is equally broken in half. As a result, the molecular weight distribution of the degraded product would not be changed. However, the significantly increase in the ***MWD*** of the sample was found in the second step of degradation. This could be resulted from completely randomly chain degradation process. Taken both molecular weight and ***MWD*** into account, the hypothesis for photodegradation of the PS foam could be confirmed. The degradation mechanism of this polymer is largely depended on the initial molecular weight. With the high molecular weight sample, the chain would primarily be broken down into half and then the short chain product would undergo randomly chain scission.

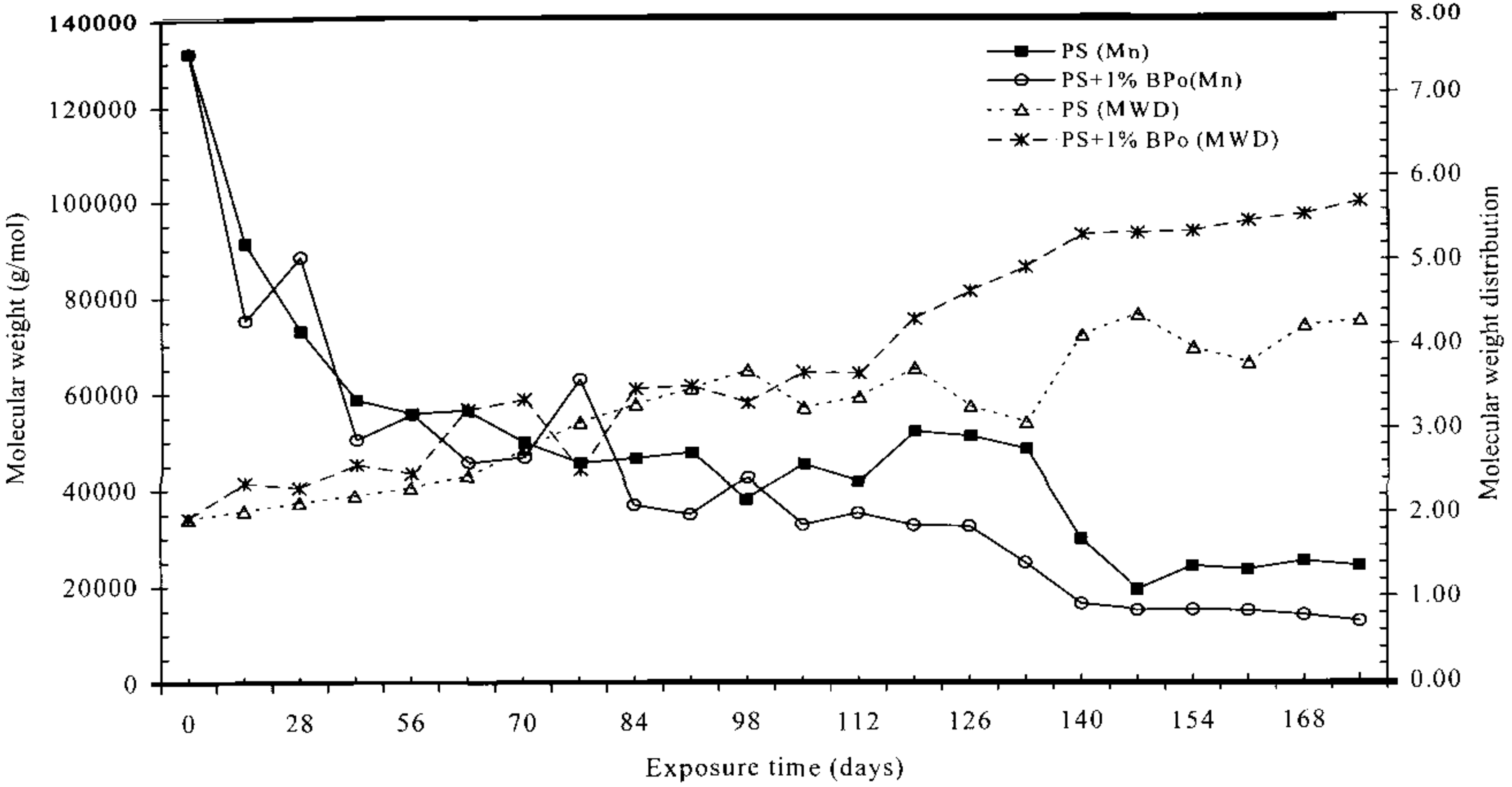
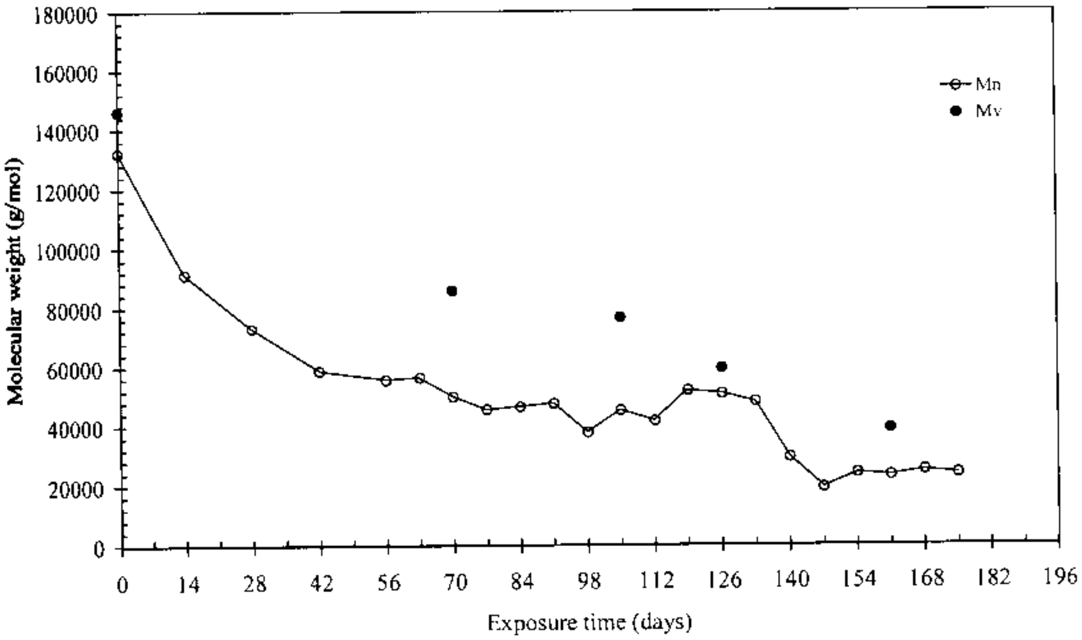


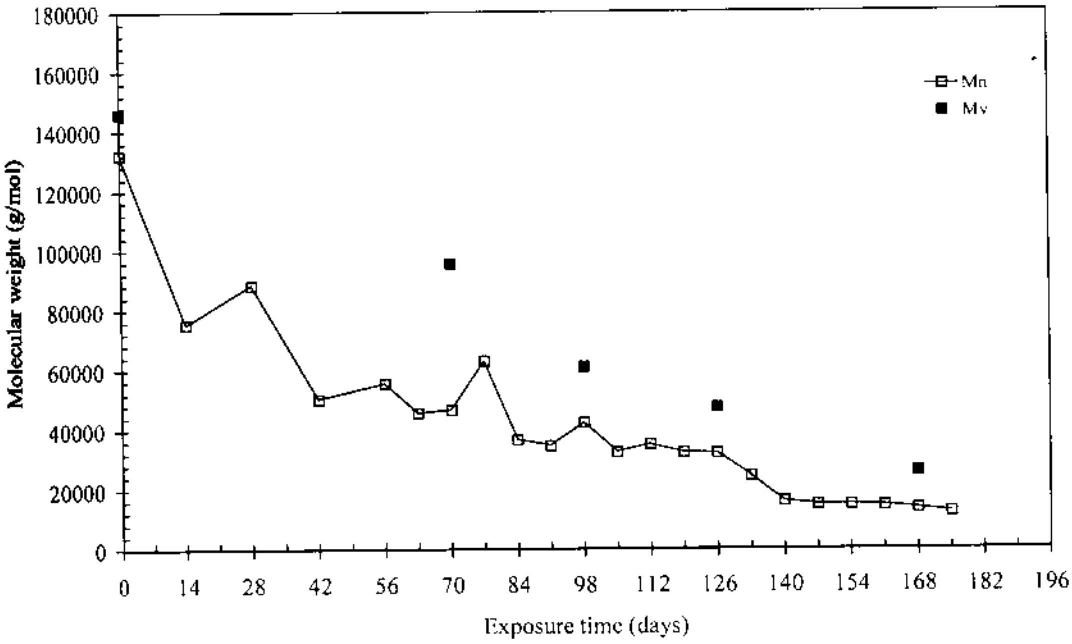
Figure 4.1 The variation in number average molecular weight and molecular weight distribution of PS and 1% Benzoyl peroxide coated PS foam sample as a function of exposure time in the natural exposure condition

There are two common initiators used in radical addition polymerization of vinyl monomers. They are Benzoyl peroxide and AIBN. Both chemicals can be decomposed by photoreaction resulting stable radical specie. It has been known that photo degradation of vinyl polymers typically occurred via radical attraction mechanism. Therefore, Benzoyl peroxide and AIBN could be used as an accelerator for the photo degradation of the PS foam. For the outdoor exposure study, only Benzoyl peroxide was investigated. Method of applying the peroxide onto specimen was described in Chapter III. The result is also shown in Figure 4.1. From the plot, the molecular weights of the foam sample were exponentially decreased with the exposure time. The trend of decreasing was similar to the degradation without accelerator. However, with the close observation it was noticed that the molecular weight reduction rate for the accelerated condition was slightly higher than the degradation rate without the peroxide accelerator. This observation will be shown and reinforced by using mathematical model simulation later on. Taken only this observation, it could be mentioned that the photo accelerator has some influence on the degradation rate.

From the plot shown in Figure 4.1, the line of molecular weight depletion with the exposure time is not completely smooth. It is often scattered. One might argue that the number average molecular weight $\overline{M}_n$ characterized by GPC, as mainly used in this study, is not constantly reliable. The value obtained by this technique is relatively to the known and narrow molecular weight PS standard. Typically, there are two types of molecular weight of polymer chain, relative and absolute values, depending on the characterization methods. The weight and viscosity average molecular weight, $\overline{M}_w$ and $\overline{M}_v$ respectively, are normally classified as absolute numbers. The magnitude orders of these three values are $\overline{M}_n < \overline{M}_v \leq \overline{M}_w$. To strengthen the result obtained from the GPC, the $\overline{M}_v$ of selected samples were analyzed by using capillary dilution viscometric technique, as explained in Chapter III, and the results are shown in Figure 4.2(*a*) and Figure 4.2(*b*). For both PS with and without accelerator, the tendency of the degradation rate monitoring by using $\overline{M}_v$ and $\overline{M}_n$ are very much similar and the two molar mass number of the identical specimen, but obtained from different methods, are closely correlated. From this finding, it could be strongly



(*a*)



(*b*)

Figure 4.2 The comparison between number average molecular weight characterized by GPC and the viscosity average molecular weight obtained from the DV method in natural exposure condition: (*a*) PS, (*b*) PS+1% BPo confirmed that the $\overline{M}_n$ analyzed by the GPC could be used to detect the degradation rate of the foam in this study.

It was also observed that all of the specimen were become brittle and eventually fallen apart into dust when their molecular weights were reduced to around 10,000 g/mol. The destruction process could also be rapidly reached when the sample subjected to external force such as strong wind and heavy rainfall. Consequently, the degraded sample which molecular weight less than 10,000 g/mol. can not be observed. *Figure 4.3 also shown the discoloration of the PS foam sample. This* phenomenon indicates that the formation of conjugate double bonds such as conjugated Polyene, Acetophenone, Benzalacetophenone, Quinimethane and the degraded short chain product are occurred during the degradation process [Rabec, 1993].

4.1.2 Accelerated Condition

It would take months to decompose the plastic sample when subjected to the natural sun light. Therefore, the high energy source known as accelerated weather was elected to simulate the decomposition time of PS foam in a shorter time. The standard weatherometer was employed. It was described earlier in Chapter III. The experimental data obtained from this study will be used to compare and predict the degradation rate of the PS foam in longer period of time. When the PS foam was exposed to the artificial weather, it molecular weight would be reduced by photodegradation reaction. As it was observed from the previous section that the samples were decomposed within 6 months. After that the specimen were collapsed due to the external natural force. Consequently, the experimental data for more than 6 months can not be obtained. By using the artificial chamber, the exposure time was setup up to 1440 hours which is equivalent to a year exposion time in the natural light.

Figure 4.4 shows the plot of number average molecular weight of the PS without Benzoyl peroxide and the PS with 1%, 2% and 3% of Benzoyl peroxide

(*a*) (*b*) (*c*)

Figure 4.3 The colors of PS foam sample in natural exposure condition (*a*) Uncoated PS foam before exposure (*b*) Uncoated PS foam at the 180th day Exposure and (*c*) Benzoyl peroxide coated PS foam at the 180th day Exposure

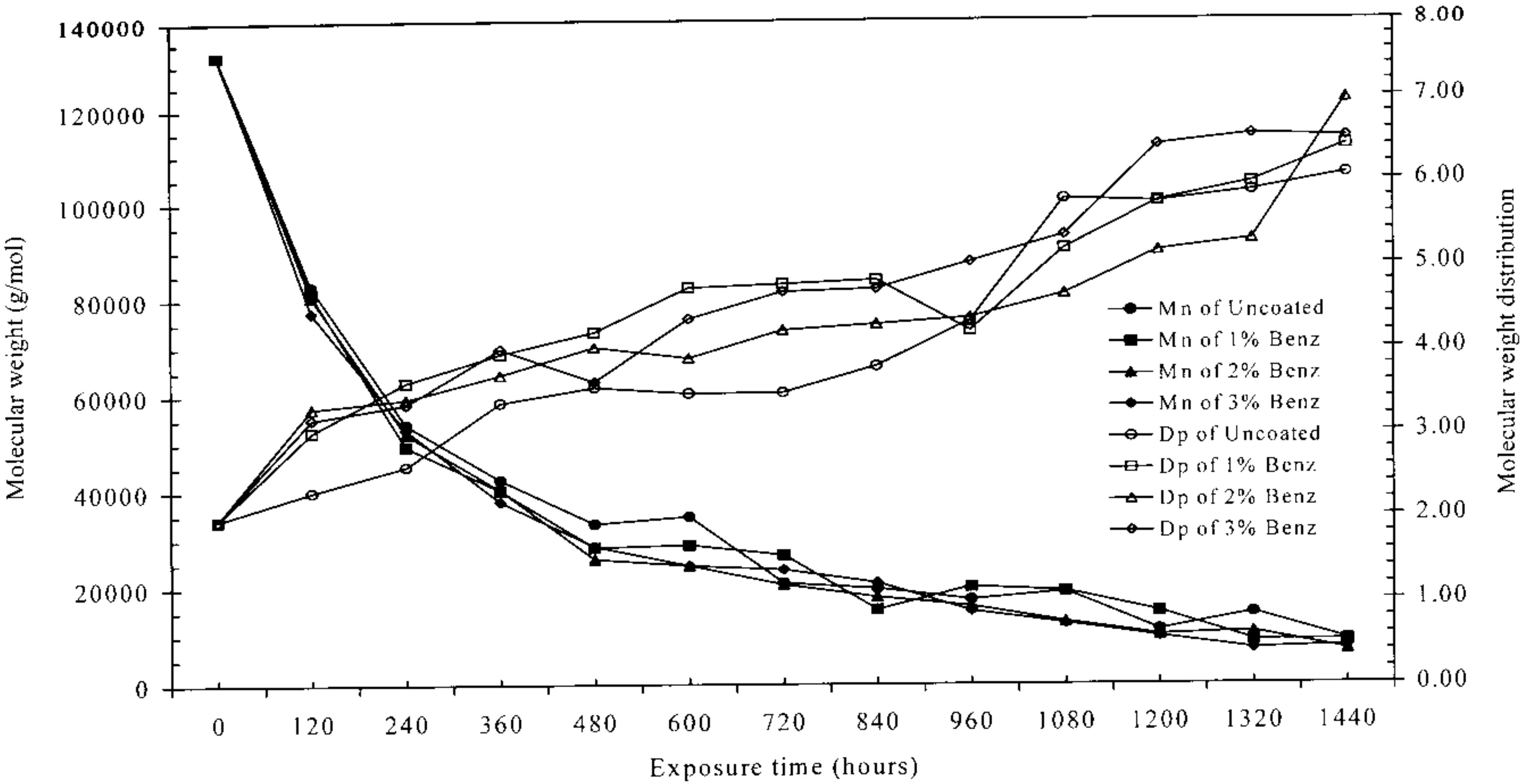


Figure 4.4 Change in the molecular weight and molecular weight distribution of Benzoyl peroxide coated PS foam in the accelerated condition

coated, respectively, with the exposure time. It is seen that the molar mass of all samples is continuously and exponentially decreased with the exposure time. At the beginning of the test, the molecular weight was rapidly reduced from 132,000 g/mol to approximately 30,000 g/mol. After that, the slowly decreasing was occurred. Finally, the chain length was reduced to around 8,000 g/mol. At this point, it was obviously seen that the foam samples were become very brittle and eventually felt apart into tiny pieces by the force of water spraying. Figure 4.4 also shows the plot of ***MWD*** of the samples with the exposure time. From the result, a constantly increased in ***MWD***, from 1.9 to approximately 6.0, the degraded specimen with the time was detected. The trend line executed from this experiment is slightly difference to those seen in open dumping degradation. It is indicated that more randomly chain scission is favored when exposed to high energy source. Similarly to those found in sun light degradation, the peroxide accelerator has slight affect on the degradation rate. The influence of the accelerators and their concentration will be discuss and obviously seen by using mathematical model later on.

It has been known that AIBN is more easily decomposed than Benzoyl peroxide. Also, the generated radical product is more stable than those obtained from the peroxide. The AIBN were also employed in this study. The molecular weight reduction of PS foam in the present of AIBN accelerator, at the concentration of 0%, 1%, 2% and 3%, respectively, with the exposure time was showed in Figure 4.5. From the plot, it was found that the molecular weights of the foam sample were decreased with the exposure time. The ***MWD*** is also constantly increased with the time. The tendency of the decreasing of molecular mass and increasing of ***MWD*** of the samples are similar to those the degradation using the peroxide as accelerator. The resembling degradation mechanism would be purposed. However, with the closed observation it was discovered that the degradation rate of the foam sample surfaced with accelerator is considerably higher than the rate of the specimen without accelerator.

During the exposure, It is also observed that both of PS foam samples were become brittle and discolored to slightly brownish as it was observed to those exposed to the sun light. The discoloration of the foam samples resulted from this experiment

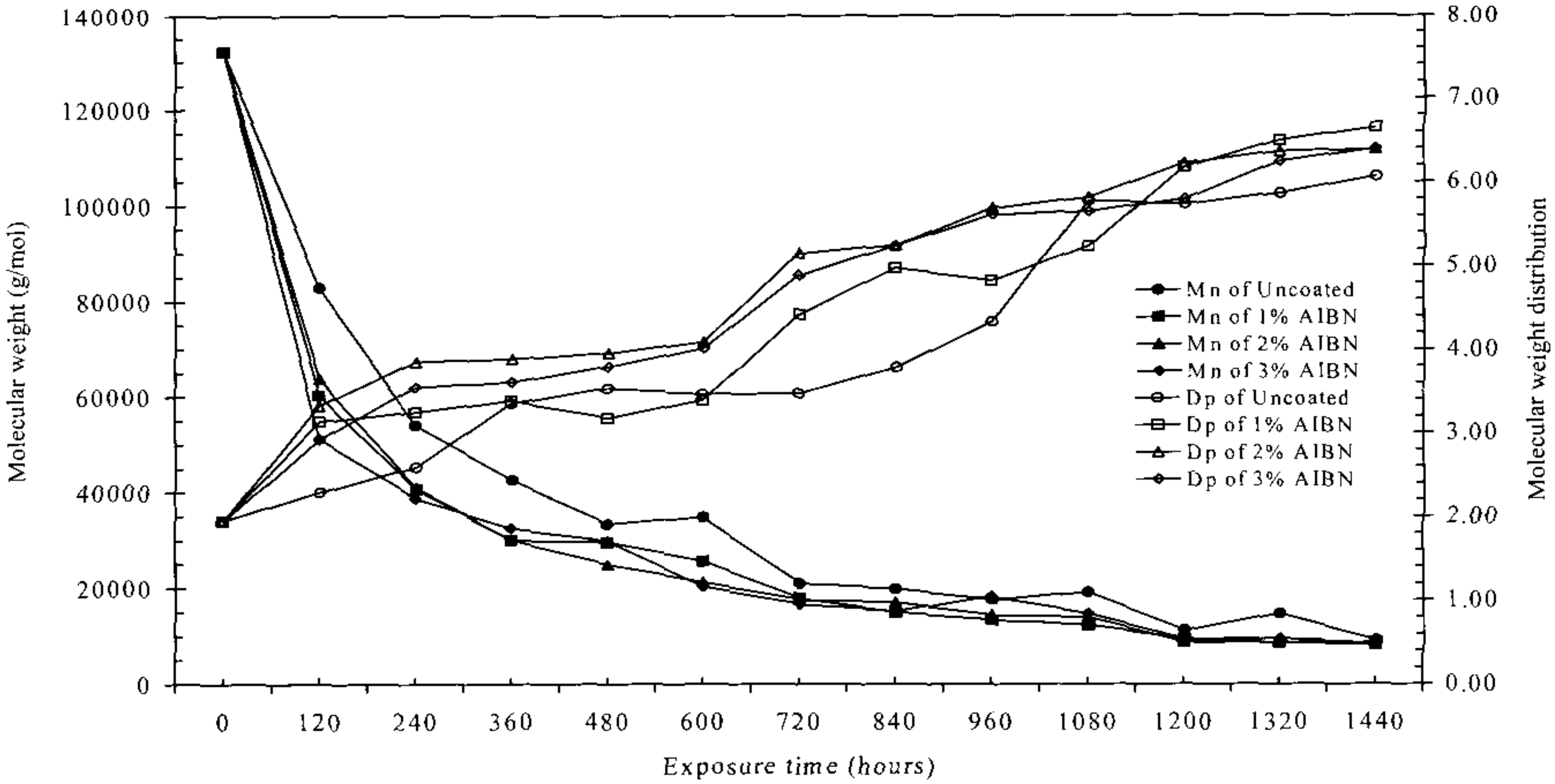
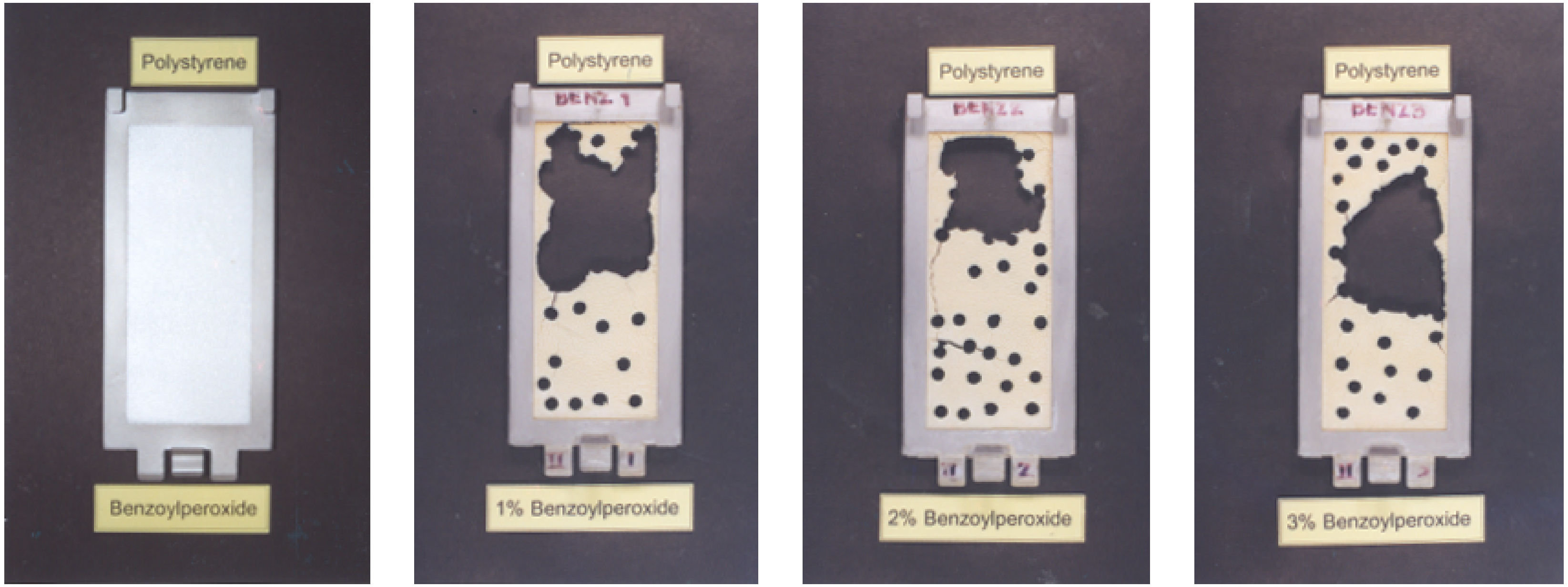


Figure 4.5 Change in the molecular weight and molecular weight distribution of AIBN coated PS foam in the accelerated condition

(*a*)

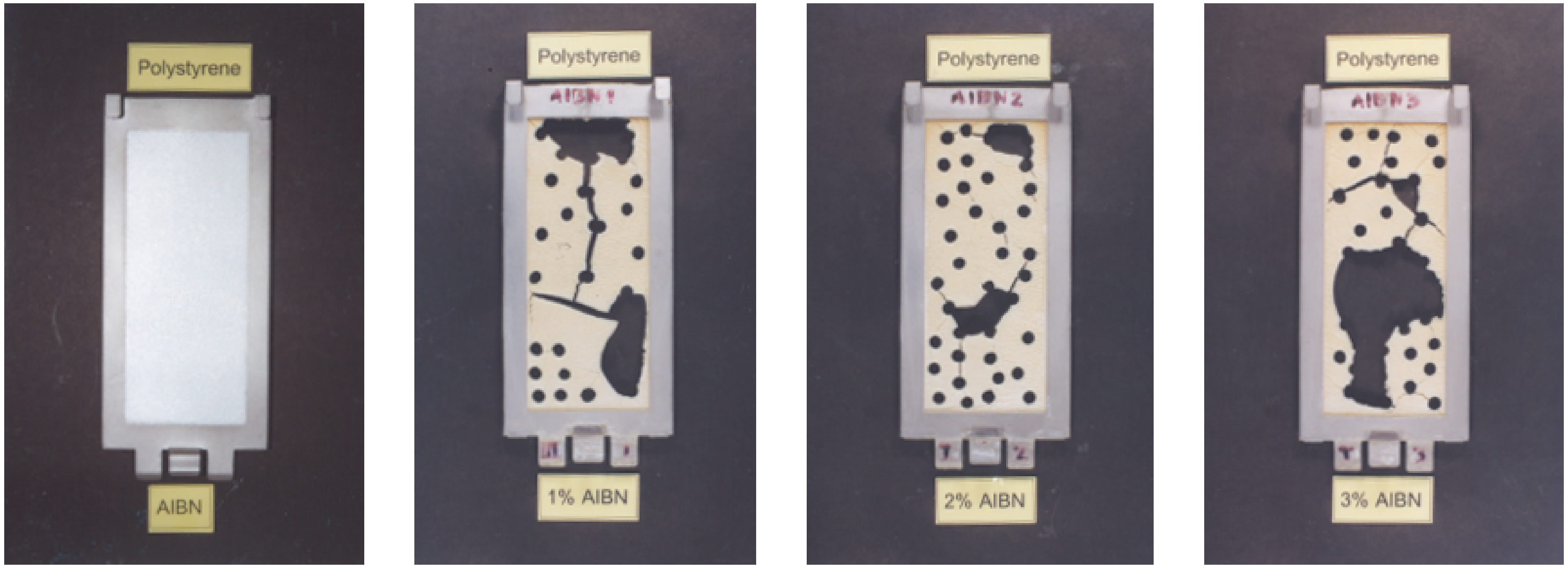
(*b*)

Figure 4.6 The colors of Uncoated PS foam sample in accelerated condition (***a***) foam before exposure (***b***) at the 1440th hour irradiation



(*a*) (*b*) (*c*) (*d*)

Figure 4.7 The colors of Benzoyl peroxide coated PS foam sample in accelerate condition **(*a*)** Uncoated PS foam before exposure **(*b*)** 1% Benzoyl peroxide coated PS foam at the 1440th hour irradiation **(*c*)** 2% Benzoyl peroxide coated PS foam at the 1440th hour irradiation and **(*d*)** 3% Benzoyl peroxide coated PS foam at the 1440th hour irradiation



(*a*) (*b*) (*c*) (*d*)

Figure 4.8 The colors of AIBN coated PS foam sample in accelerate condition (***a***) Uncoated PS foam before exposure (***b***) 1% AIBN coated PS foam at the 1440th hour irradiation (***c***) 2% AIBN coated PS foam at the 1440th hour irradiation and (***d***) 3% AIBN coated PS foam at the 1440th hour irradiation were also illustrated in Figure 4.6 to Figure 4.8 for non-accelerated, peroxide accelerated and AIBN accelerated, respectively. These results indicate that the conjugate double bond and such as Polyene, Acetophenone and other degraded short chain product are spontaneously occurred during the chain destruction process.

Normally, the quantity of accelerator cooperated on the sample would had a significant effect on the photo degradation rate of the PS foam. Having a close observation on Figure 4.4 and Figure 4.5, which are the degradation rate of the sample accelerated by the peroxide and AIBN, the results indicate that there is no significantly different in the degradation rate of the foam with increasing the concentration of accelerator, especially, when it was treated with the peroxide. Again, by using the mathematical modeling, the dependency of the accelerators on the rate will clearly seen. The discussion of the mathematical model will be shown in the following section.

From the beginning of the discussion, One could be pointed out that the degradation of PS foam in opened atmosphere and also in the accelerated condition, whether with or without accelerators, is mainly occurred by chain scission process. The random chain shorten is obviously seen when the molecule is reduced to smaller in molecular weight. The minimum molecular weight of the specimen, before it becomes brittle and finally falls apart into tiny dust, is approximately 8,000 g/mol. Increasing in the degradation rate of the sample has been observed where the accelerators, Benzoyl peroxide and AIBN, are employed. These accelerators could generate more highly reactive radical species by the photolysis and they would then attract on the PS chain. Subsequently, the polymer molecule will either be broken down or form the active site on the chain backbone. The latter would then increase the probability of the degradation process.

On the other hand, it has evidence that the accelerators could initiated the crosslinked structure through the formation of double bond in the vinyl polymer, especially for the polyehtylene, during degradation [Kaczmarek *et al.* (2000)]. The network polymer product would not dissolve in any solvents. In this study, the crosslink mechanism is not found.

The proposed mechanism of free radical chain degradation reaction of PS polymer was given by Cheremisinoff and his coworker, and it is shown in Figure 4.9 [Cheremisinoff and Dekkar (1989)].

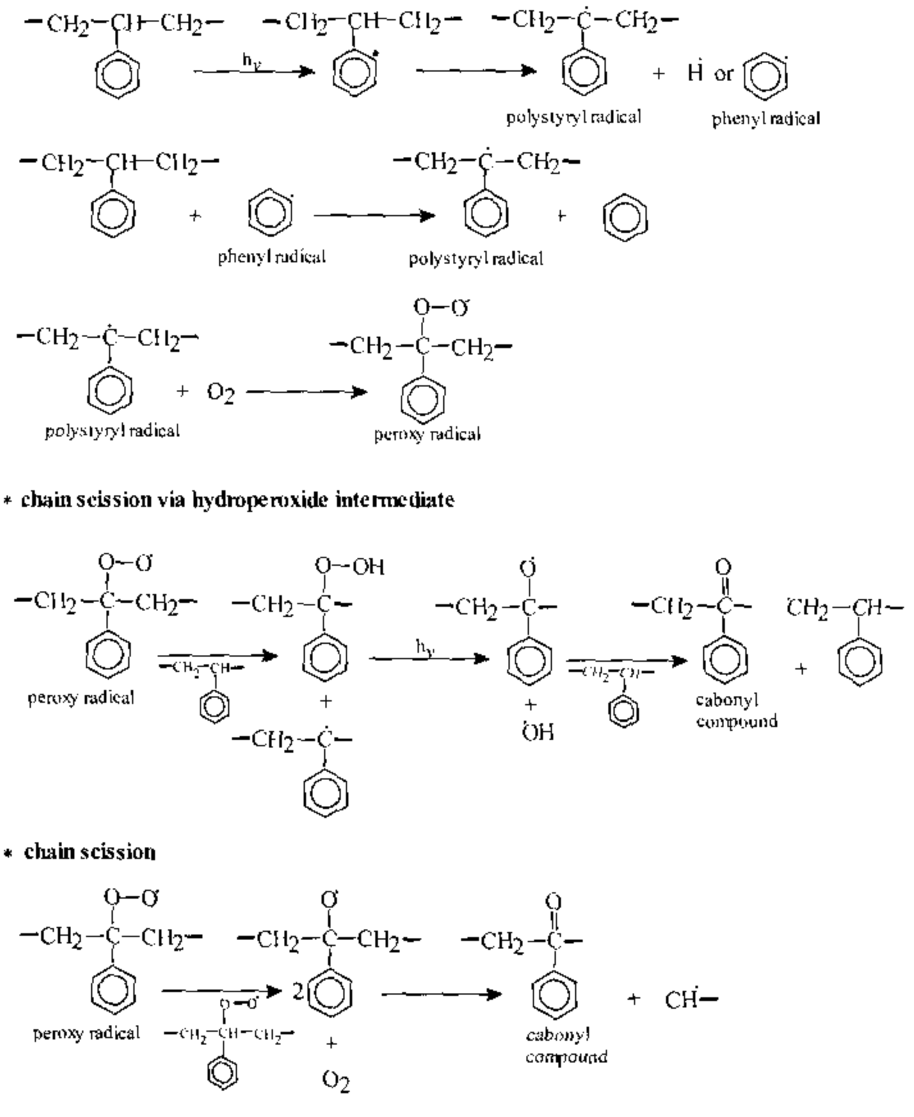
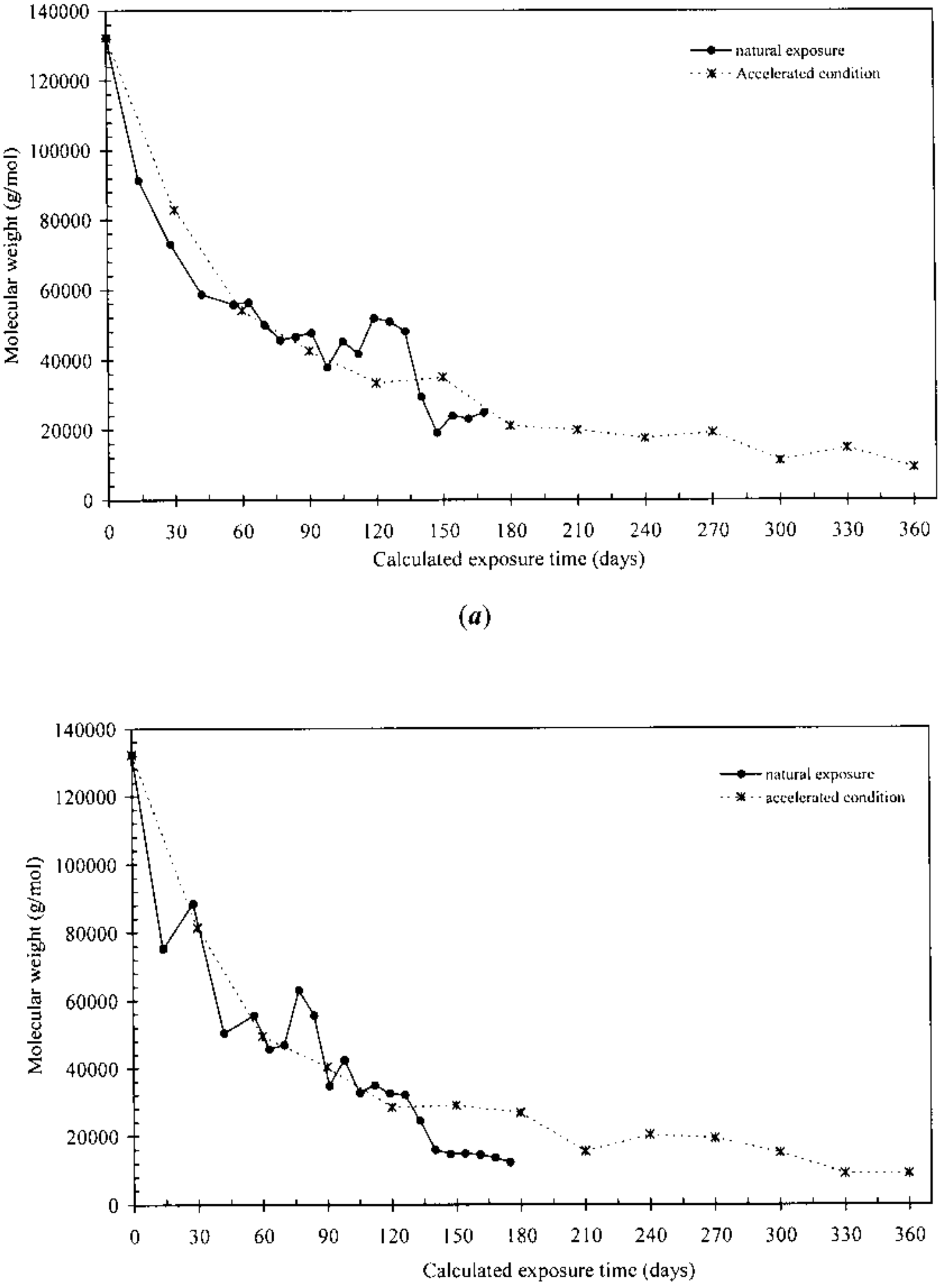


Figure 4.9 Mechanism of photo-oxidation reaction of Polystyrene
[Source: Cheremisinoff and Dekkar (1989)].

4.1.3 Comparison between Accelerated and Natural Exposure Data

Most of polymer products would take years to be degraded in the open-air environment. If the accelerated weather condition, in the laboratory, can be used to accelerate the decomposition time and the collected data are somehow equivalent to those obtained in the actual condition, it would be useful for the scientists and engineers. Consequently, the design processes for managing these solid wastes would be shorten. One of the objectives of this study is to find out that the degradation behavior of the PS foam in accelerated atmosphere is equivalent to those found in the natural atmosphere. If it does, as mention earlier, the result would be used to design and determine the management processes for the PS foam. From the calculation shown in Appendix A, it is found that 120 hours of exposure time in the accelerated chamber was equivalent to a month of natural exposing. Figure 4.10(*a*) and 4.10(*b*) show the degradation behavior of the foam without and with 1% peroxide coated, respectively, when they were naturally exposed to the sunlight compare with ones that were degraded in the accelerated chamber. The X-axis is represented the calculated exposure time according to equation shown in chapter III. For the sample with no accelerator, the molecular weight reduction line of the open air degradation is very similar trend to those found in the accelerated condition except at the exposure period of around 4 months where the molecular weight of the natural exposed samples are scattered. It could be due to the seasonal fluctuation as the outdoor experiment began in the October time which is the end of rainy season in Thailand and the test went for a period of 3 months to the mid of winter time, January, where the temperature is lower and also the day time is normally shorter than the summer season(The average temperature in the winter and summer season are 24.1 and 29.2, reapectively). According to this phenomenon, the degradation rate was slow down with in the wintertime and further increasing in the summer time, the 5th month of exposure period. The similar trends were also observed for the peroxide accelerated study.

If the molecular weight data of the foam sample at the equivalent time for the natural and accelerated condition were identical, it would indicate that the degradation of PS foam in natural environment can be predicted by using the data tested in the



(*a*)

(*b*)

Figure 4.10 A plot of number average molecular weight at the equivalent time between accelerated and natural condition of (*a*) Uncoated PS foam and (*b*) 1% Benzoyl peroxide coated PS foam accelerated condition. This statement can be clearly solved by the mathematical mean that;

$$\frac{\sum(x_i - y_i)}{N} = 0 \qquad (4.1)$$

$$\frac{\sum x_i}{N} - \frac{\sum y_i}{N} = 0 \qquad (4.2)$$

then $$\overline{X} - \overline{Y} = 0 \qquad (4.3)$$

where x_i = the molecular weight of the sample obtained from natural exposure at the given equivalent time.

y_i = the molecular weight of the sample obtained from accelerated chamber at the given equivalent time.

and N = number of data points.

By considering the statistical method, the difference in the average mean values, $(\overline{X} - \overline{Y})$, for the experimental data obtained from natural and accelerated exposure, respectively, can be tested. Typically, two statistical hypothesizes, null(H_o) and alternative(H_1) will be identified as shown below;

If H_0: $\overline{X} - \overline{Y} = 0$, it means that x and y is analogous,

and if H_1: $\overline{X} - \overline{Y} \neq 0$, it means that x and y is, somehow, difference.

By using the 2-tail T-test method, the t value can be computed. It is known that if t value fall into the range of $-t_{1-\alpha/2} < t < t_{1-\alpha/2}$ the H_0 is accepted. However, the H_0 would be rejected when $-t_{1-\alpha/2} > t > t_{1-\alpha/2}$. In this study the degree of confidential to accept H_o is set at 95% and, therefore, the level of the significant(α) is 5%. The null hypothesis(H_0) will be accepted when the calculated t is fall between $t_{0.975}$ and $-t_{0.975}$. The calculated t can be determined by using the equation 4.4 as show below.

$$t = \frac{\left(\overline{X} - \overline{Y}\right)}{S_p\sqrt{1/n_x + 1/n_y}} \tag{4.4}$$

$$S_p = \sqrt{\frac{(n_x - 1)S_x^{\ 2} + (n_y - 1)S_y^{\ 2}}{\left(n_x + n_y - 2\right)}} \tag{4.5}$$

and $$S_i = \frac{\sum\left(x_i - \overline{X}\right)^2}{n_i - 1} \tag{4.6}$$

where S_i is the variant of i-data and $\left(n_x + n_y - 2\right)$ is the degree of *freedom used in the test.*

Only seven pair of data points, including the initial molecular weight, at the equivalent degradation time was illustrated. in Table 4.1. The table shows the molecular weight of the foam with and without peroxide catalyzed at the given time obtained by the natural and accelerated testing, respectively. By using the equation 4.4 and the degree of freedom of 12 the t values were computed. They are –0.019 and 0.059 for the foam with no peroxide coated and the foam with 1 % peroxide coated, respectively. From the statistical table for the t-test as shown in appendix C, it illustrates that the critical value of t at degree of freedom 12 and level significant of 5%, $\alpha/2 = 0.025$, are ±2.18. In comparison between the calculated t and the value obtained from the referee table, it is found that the calculated t is felt onto the hypothesis accepting region, $\pm t_{(1-\alpha/2)}$. As the result, H_0 is accepted. It means that the experimental data obtained from natural exposure is analogous to the ones resulted from the test performed in acceleration chamber. The preliminary conclusion can be stated that the degradation rate of the PS foam accomplished in the artificially accelerated atmosphere is similar to those done in the normal opened condition.

By using SPSS commercial computer programming to assist and confirm the statistical calculation shown earlier, the exact conclusion was encountered. According to the SPSS calculation, the level of significant(α) or, on the other word, the probability(p), will be identified. If p of the absolute value of calculated t, $|t|$, which is also calculated from the equation 4.4, is greater than the given level of significant, then, the hypothesis H_0 will be accepted. By using the computer programming, shown in appendix B, the p of the data for the foam sample without and with 1% peroxide are 0.985 and 0.954, respectively. The applied level of significant for this test is 0.05 Therefore, it is found that the two computed values are greater than p at given level of significant. Taken the result from the previous ordinary t-test and also from the SPSS method, it could strongly suggest that the degradation data of the PS foam experimented in the normal open-air atmosphere are identical to those done in the accelerated chamber. Statistically, this statement is true with the 95 % degree of confidence.

Table 4.1 The number average molecular weight of the foam sample obtained from the natural and accelerated condition experiment

Calculated time (months)	Natural condition (x_i)		Accelerated condition (y_i)	
	PS	PS + 1% peroxide	PS	PS + 1% peroxide
0	132210	132210	132210	132210
1	73079	88473	82850	81389
2	55848	55623	54076	49501
3	46600	55623	42571	40376
4	41738	35106	33364	28442
5	29415	15983	34883	28943
6	*24811*	*13595*	*21006*	*26845*
Mean Average	57280	56659	57617	55387

4.1.4 Degradation Modeling

The degradation of the PS foam by photoinitiation is a complex process because it has many factors involved. The main factors are weather conditions such as light intensity, exposure time, concentration of accelerator or other additives in the foam and the molecular characteristic of the foam, *e.g.*, molecular weight. Only the concentration of accelerator and molecular weight are included in the degradation model. The main objective of the mathematical modeling is to obtain the rate constant and the reaction order of photodegradation of the foam.

In this study, the degradation model is erected under the assumption that the degradation of the foam occurs because of molecular chain scission as mention from previous section. The rate of chain scission of the polymer molecules depends on both type and it concentration of the accelerator used. It is also depends on initial the molecular weight of the foam. In this research work, the average chain length($\overline{X}_n$) is used in place of the number average molecular weight($\overline{M}_n$). It can be simply calculated by the dividing the number average molecular weight of PS by the molecular weight of monomer unit, styrene, (108 g/mol).

Therefore, the mathematical model, which can explain the degradation of the PS foam, is shown in equation 4.7.

$$-\frac{d\overline{X}_n}{dt} = kC^m\overline{X}_n^{\,n} \qquad (4.7)$$

where $-\frac{d\overline{X}_n}{dt}$ = the reduction rate of the average chain length of the PS foam

C = the concentration of accelerator or additive (% wt)

t = the exposure time

k = rate constant

and m and n = order of reaction with respect to accelerator and average chain length of the foam, respectively.

From the addition polymerisation reaction, it is known that the Peroxide and AIBN can be decomposed to the radical species. The similar phenomenon would be occurred in the degradation process. It is also found in the polymerisation that the *steady state condition*, where the initiation rate is equal to the termination rate, is taken place. As the result, the concentration of highly reactive radical is constant. As the photodegradation of the PS foam is the depolymerisation process by radical specie, the concentration radical specie is also assuming constant. Consequently, the C^m is constant. Then, the equation 4.7 can be simplified as shown below;

$$-\frac{d\overline{X}_n}{dt} = k'\overline{X}_n^{\,n} \tag{4.8}$$

where k' = the rate constant

$= k \times C^m$

and n = the reaction order respectively to the average chain length of polymer

Integration of Equation 4.8 with the exposure time starting from $t = 0$ to $t = t$ and it is given rise to equation 4.9 which is the function of average chain length with exposure time and order of reaction.

$$\overline{X}_{n_t}^{\,(1-n)} = \overline{X}_{n_0}^{\,(1-n)} + (n-1)k't \tag{4.9}$$

where

$\overline{X}_{n_0}$ = the average chain length of the foam at time t = 0 or the initial average chain length

$\overline{X}_{n_t}$ = the average chain length of the PS foam at time t = t

In order to obtain the reaction rate constant, k', and reaction order, n, there are two common methods for resolving the equation. The first one would be the statistical approach. The least square and numerical methods were employed. The basic principle of least square method is shown in equation 4.10.

$$e^2 = \sum_{i=1}^{N}\left(\overline{X}_{n_i} - \overline{X}_{n_{model}}\right)^2 \tag{4.10}$$

where e = The total difference between $\overline{X}n$ obtained from the experiment($\overline{X}n_i$) and the model($\overline{X}n_{model}$)

$\overline{X}n_i$ = The average chain length of the sample at exposure time t_i

$\overline{X}n_{model}$ = The predicted average chain length used in the model as shown in equation 4.9

Substitution of equation 4.9 into 4.10 resulting that;

$$e^2 = \sum_{i=1}^{N}\left[\overline{X}n_i - \left(\overline{X}n_0^{(1-n)} + (n-1)k't\right)^{\left(\frac{1}{1-n}\right)}\right]^2 \qquad (4.11)$$

Determining the first order derivative of equation 4.11 with respect to k'or n will give rise to the function of $\sum\overline{X}n_i$, $\sum t_i$, n and k'that must be zero as shown in equation 4.12. This could be done by using the numerical differentiation method [Buchanan and Turner (1992)].

$$f\left(\sum\overline{X}n_i, \sum t_i, n, k'\right) = 0 \qquad (4.12)$$

Substitution of the data obtained from the experiment, $\overline{X}n_i$ and t_i, into equation 4.12, the parameter k' and n can be solved. It can also be done by the numerical analysis such as iteration method [Buchanan and Turner (1992)].

Alternatively, the most simple method can be applied to approximate the k' and n. It is called "*the molecular reduction rate*" in this present work. The basic fundamental of this method is that the approximated chain reduction rate(R_{ap}) is obtained by dividing the change of the molecular chain length of the two consecutive exposure time by the time interval as shown below.

$$-\frac{d\overline{X}n}{dt} \cong -\frac{\Delta\overline{X}n}{\Delta_t} \cong R_{ap} = \frac{\overline{X}n_t - \overline{X}n_{t+\Delta t}}{\Delta_t} \tag{4.13}$$

Therefore, the equation 4.8 can be simplified as following;

$$R_{ap} = k'\left(\overline{X}n,_t\right)^n \tag{4.14}$$

where

$$\overline{X}n,_t \cong \frac{\overline{X}n_t + \overline{X}n_{t+\Delta t}}{2} \tag{4.15}$$

Taking logarithm into equation 4.14, it is then given rise to the linear equation form, $Y = aX + b$, as shown below.

$$log\ R_{ap} = log\ k' + n\ \ log\overline{X}n,_t \tag{4.16}$$

where $Y = log\ R_{ap}$

$X = log\overline{X}n,_t$

$a = n$

and $b = log\ k'$

The order of reaction, n, and the rate constant, k', can be derived from slope and Y-axis interception of the graph plotted between $log\overline{X}n,_t$ and $log\ R_{ap}$, respectively. The molecular weight reduction rate method is employed in this study.

Table 4.2 summarizes the values of $log\overline{X}n,_t$ and $log\ R_{ap}$ of the 1% AIBN coated foam sample in the acceleration chamber. The linearly plot of these two sets of data is illustrated in Figure 4.11. By using the statistical linear regression analysis, it was found that the reaction order(n) and the rate constant(k') of this photodegradation are 1.96 and 8.32×10^{6}, respectively.

Table 4.2 Average chain length($\overline{Xn}$), $\log R_{ap}$ and $\log \overline{X}_{n,t}$ of the 1% AIBN coated PS foam under accelerated experiment

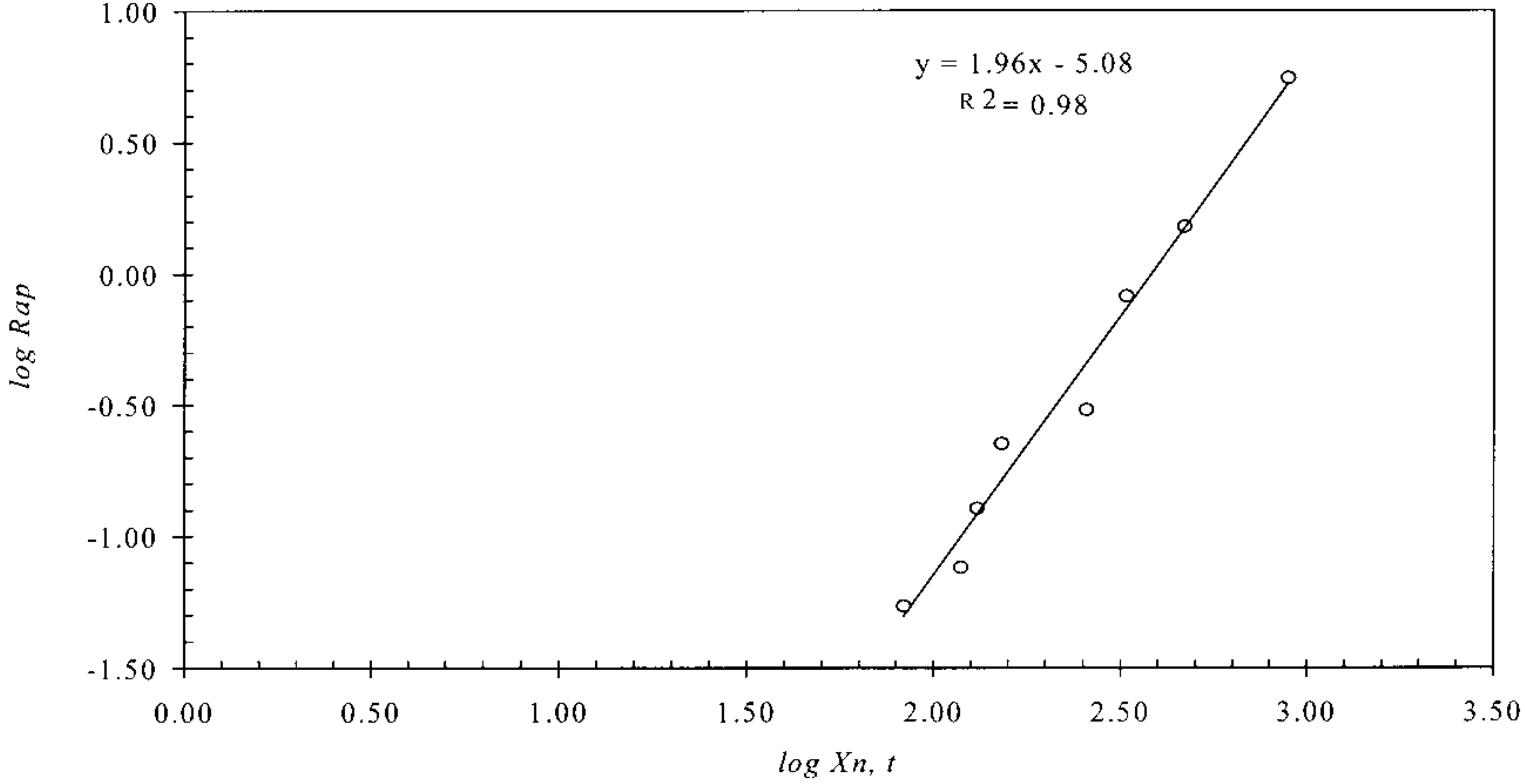
Exposure time (hours)	$\overline{Mn}^{a}$	$\overline{Xn}$	$\log R_{ap}$	$\log \overline{X}_{n,t}$
0	132210	1224	-	-
120	60331	559	0.744	2.950
240	40730	377	0.180	2.670
360	30042	278	-0.084	2.515
480	29611	274	-1.478	2.441
600	25674	238	-0.517	2.408
720	17871	165	-0.220	2.304
840	14948	138	-0.647	2.182
960	13295	123	-0.894	2.116
1080	12310	114	-1.119	2.074
1200	9337	86	-0.639	2.001
1320	8633	80	-1.265	1.920
1440	8609	80	-2.732	1.902

Remark: ^{a} obtained from the GPC technique

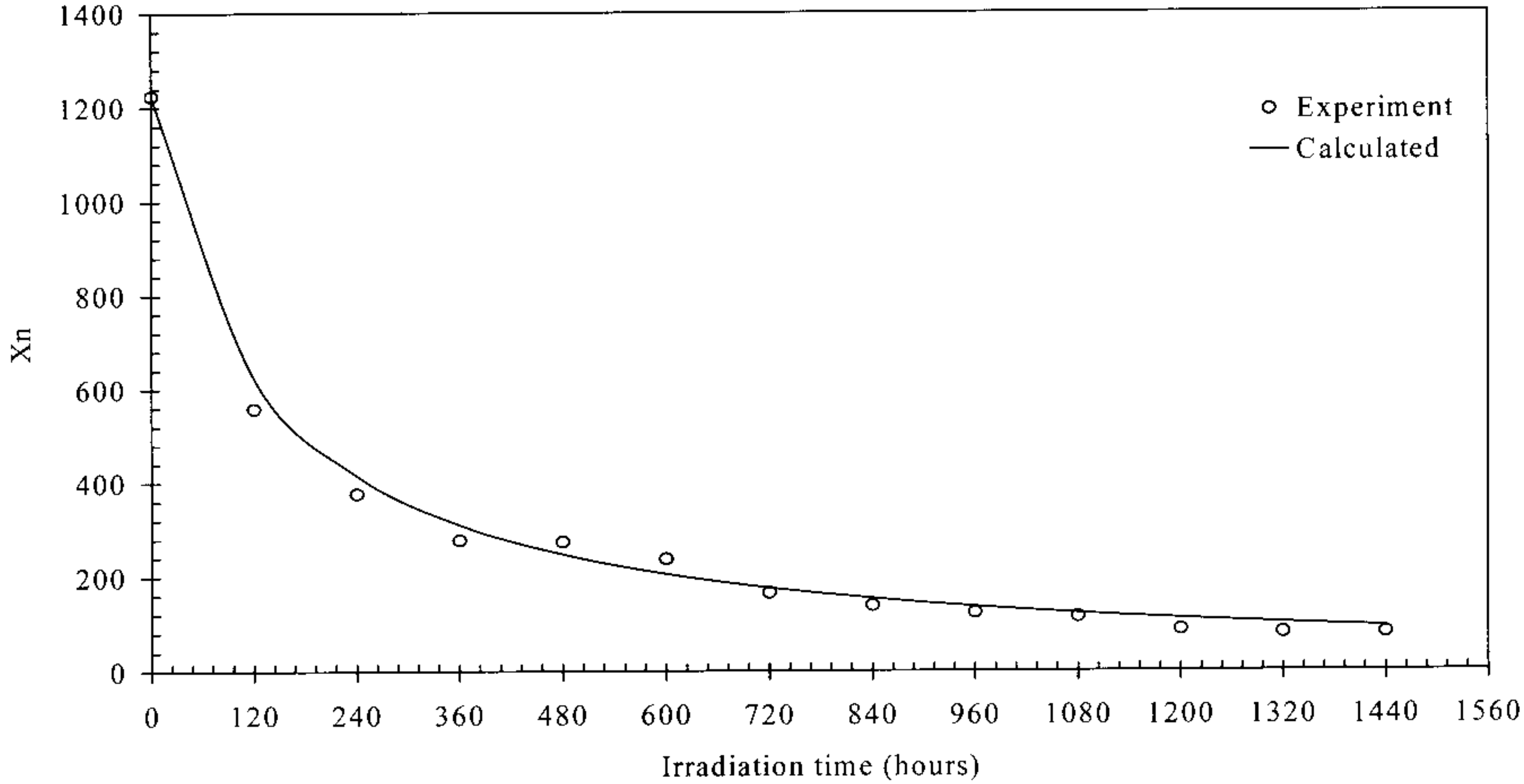
Substitution of n and k'resulted from the model into Eq. 4.9 gives rise to the equation 4.17 which is the function of the average chain length($\overline{X}_{n,t}$) and the exposure time(t) which is referred to the model equation of photodegradation of the PS foam.

$$\overline{X}_{n_t}^{(1-1.96)} = \overline{X}_{n_0}^{(1-1.96)} + (1.96 - 1) \times 8.32 \times 10^{-6} t \qquad (4.17)$$

Figure 4.12 shows the plot of the average chain length of the sample against the exposure time derived from the actual experiment and also from the model equation, respectively. The plot indicates that the model equation is closely related to the experimental data. By using the statistical parameter, the correlation coefficient(r), which is calculated according to equation 4.18, is 0.997. From the value obtained, the conclusion can be made that the mathematical photodegradation model of the PS foam purposed in this work is reasonably acceptable.



gure 4.11 Curve fitting to determine the reaction order and reaction rate constant for 1% AIBN coated PS foam in accelerated condition



igure 4.12 The molecular weight of 1% AIBN coated PS foam predicted by using the model compare with the molecular weight observed in accelerated condition experiment

$$r = \frac{\sum\left(x_i - \bar{X}\right)\left(y_i - \bar{Y}\right)}{\sqrt{\sum\left(x_i - \bar{X}\right)^2}\sqrt{\sum\left(y_i - \bar{Y}\right)^2}} \tag{4.18}$$

where x_i = the calculated average molecular chain length by using the degradation model

y_i = the average molecular chain length obtained from the experiment

The modeling method as described above is also applied for the degradation of the foam samples both treated and untreated with accelerators and exposed to the natural and in the acceleration chamber, consecutively. The order of reaction(n), the rate constant(k'), the correlation coefficient(r) and also the half-life($t_{1/2}$) for those samples are resolved and summarized in Table 4.3.

Table 4.3 Summarizing of the model value of n, k', r and $t_{1/2}$ of the PS foam in various degradation conditions

Sample	Reaction order (n)	Reaction rate constant (k')[a]	Half life ($t_{1/2}$)[b]	Correlation coefficient (r)
Natural exposure:				
neat PS	1.58	3.51×10^{-4}	119	0.950
PS+1% BPo	1.75	1.29×10^{-4}	84	0.938
Accelerated condition:				
neat PS	1.78	1.95×10^{-5}	441	0.997
PS+1% BPo	1.82	1.82×10^{-5}	348	0.995
PS+2% Bpo	1.91	8.91×10^{-6}	359	0.998
PS+3% Bpo	1.95	6.92×10^{-6}	343	0.998
PS+1% AIBN	1.96	8.32×10^{-6}	264	0.997
PS+2% AIBN	2.02	6.17×10^{-6}	228	0.997
PS+3% AIBN	2.28	1.78×10^{-6}	119	0.995

[a] Unit of the reaction rate constant are day^{-1} and hour^{-1} for natural and accelerated condition, respectively.

[b] Unit of the half life are day and hour for natural and accelerated condition, respectively.

From the result obtained in Table 4.3, it is shown that the neat sample which were exposed to the sunlight has slightly higher order of reaction(***n***) than those foam degraded under the artificial light source. The similar figures are also observed for the 1% peroxide coated sample. However, the rate constants are found in reverse order to the ***n***. The small differences in these calculated values derived from those two exposure conditions are due to the fact that there is more uniform and continuity of the indented energy in the chamber than the natural sunlight. This hypothesis is reinforced by the correlation coefficient of the experiment performed in the environmental chamber, which closes to 1.0.

Nevertheless, the results also show that the ***n*** was increased with the increase of the accelerator concentration of both peroxide and AIBN. Vice versa, the ***k′*** was decreased with the increase the amount of accelerators. Figure 4.13 shows the plot of ***n*** and concentration of the accelerators. It is obviously seen that ***n*** was linearly depended on the concentration. This result indicates that higher in accelerator concentration would generate higher concentration of radical species. This highly reactive chemical would accelerate the photodegradation reaction and, hence, the order of reaction. In comparison, AIBN has more strongly dependency than the peroxide. It is well known that the radical generated from the photo decomposition of AIBN has higher in stability than the radical decomposed from the Benzoyl peroxide. Therefore, it has superior in life-time. According to the study by Kaczmerak *et al.* (2000), they reported that the affectivity of photoinitiator on the degradation of polystyrene was depended on its chemical structure, concentration, life-time of its excited states and stability of radicals formed during their photolysis.

Considering the correlation coefficient(***r***) of all samples, it is closed to 1.0 except for the data obtained from the natural sunlight. This finding again suggests that the degradation model is somehow in agreement with the experiment and can be accepted. More over, it could be pointed out that the degradation of PS foam in the open-air atmosphere is largely depended on the concentration of the accelerators.

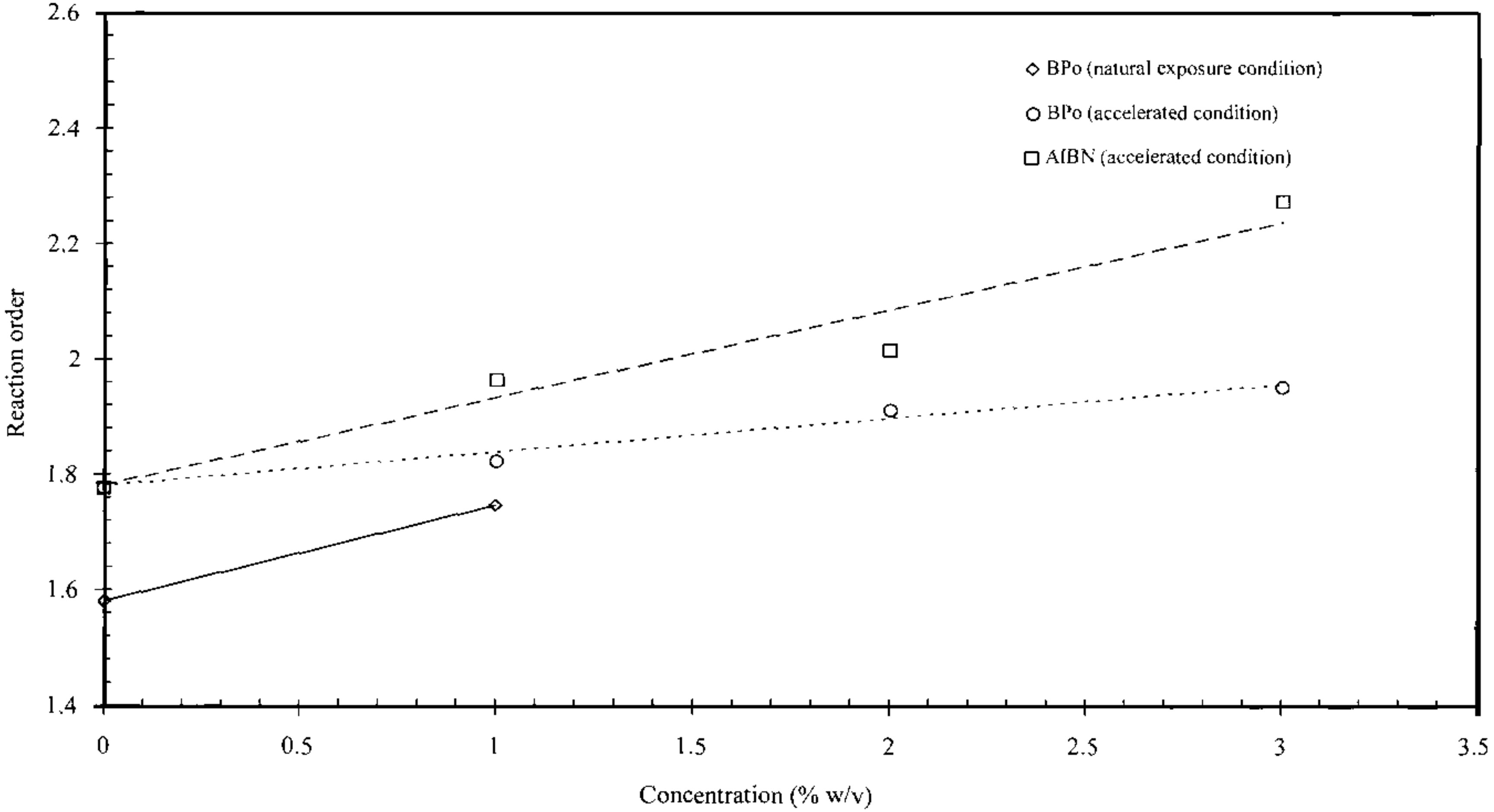


Figure 4.13 Effect of accelerator concentration on the reaction order in the open air dumping condition

4.2 Degradation in Landfills

Most of the municipal solid wastes would be disposed in landfills. It has been known that under landfill condition, the solid waste is degraded by anaerobic bacterial reaction. In the reaction, nitrate and sulfate is normally added as the supplementary nutrition. They are acted as electron acceptor for the anaerobic bacterial degradation [Tchobanoglous *et al.* (1993)]. In this research work, the effects of inorganic nitrate and sulfate in the landfill topsoil and also effect of surface area, by mean of sample size, of the solid foam on the degradation process were investigated.

4.2.1 Effect of Surface Area

As described earlier that two differences physical form of samples, coarse and fine crushed, were employed in this study. Figure 4.14 shows the changes in the molecular weight of coarse and fine crushed of the PS foam samples after burial in landfill site for a period of 24 weeks. The plot shown that there is no significantly change in molecular weight of the sample for both coarse and fine crushed specimens. This result suggests that the PS foam can not be degraded with in 24 weeks. Increasing in the surface area also does not affect on the degradation rate.

The above statements are reconfirmed by using statistical argument, T-test, as previously described in Eq. 4.1 - 4.6. Also, if the level of significant(α) of the test is 0.05 and the statistical hypothesizes is as following;

If $H_0: \bar{X} - \bar{Y} = 0$, it means that the changing in molecular weight of coarse and fine crushed samples are not observed,

but if $H_1: \bar{X} - \bar{Y} \neq 0$, it means that the changing in molecular weight of coarse and fine crushed samples are clearly observed.

As explained in section 4.1.3, the statistical value of the T-test indicates that the Null hypothesis, H_0, will be accepted if the calculated t from equation 4.4 falls

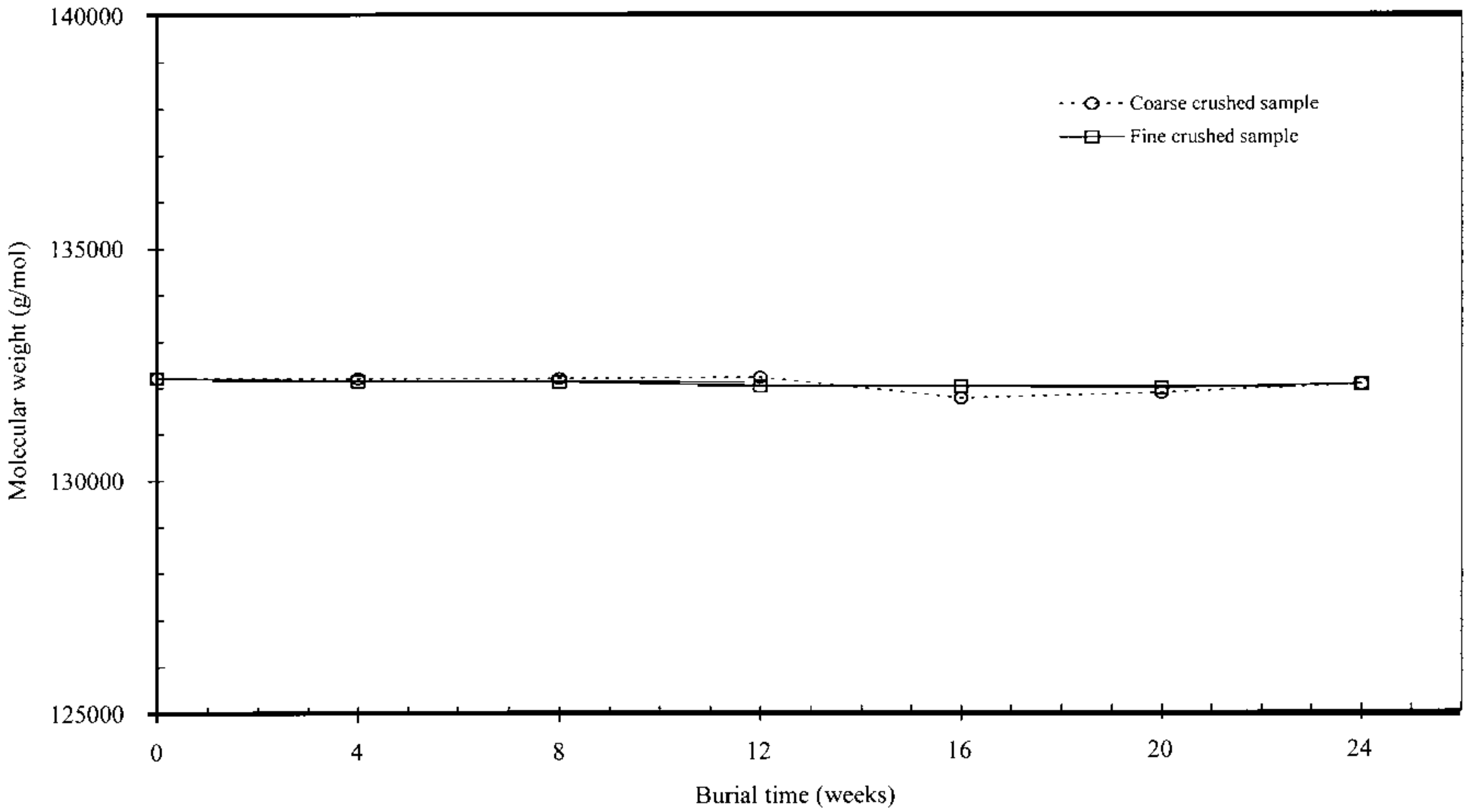


Figure 4.14 The variation in number average molecular weight of coarse and fine crushed PS foam with the burial time

into the range of $-t_{1-\alpha/2} < t < t_{1-\alpha/2}$. Vice versa, the H_o is rejected. From the statistical table of the probability distribution t-curve as shown in appendix C, at the $\alpha = 0.05$ and degree of freedom (v) equal to 12, the $\pm t_{1-\alpha/2}$ are ± 2.18. From the experimental data, calculated t is -0.096 which is felt into the range of $-2.18 < t < 2.18$. Based on this statistical calculation, the H_o is accepted. With the degree of 95% reliability, the study outcome would strengthen the fact that increasing of surface area of the sample does not have any significant affect on the PS foam degradation when it was buried in the landfill cell for a period of six months.

4.2.2 Effect of Inorganic Nitrate and Sulfate

As mentioned earlier that inorganic nitrate and sulfate are occasionally added as the supplementary nutrition for anaerobic bacterial in the landfill process. Figure 4.15 and 4.16 show the molecular weight of the foam samples, both coarse and fine crushed, in landfill cell against the burial time for a period of six months. The concentrations of the inorganic nitrate and sulfate added into the topsoil were also varied from 0, 200, 300 and 500 ppm, respectively. The plots show that the molecular weight of the PS foam does not change with in the 6 months of the burial time. They are also reviewed that both type and as well as the concentrations of the supplementary nutrition do not have significant affect on the degradation rate of the samples. As it was concluded in the previous section that the surface area of the samples also do not have any influent on the degradation reaction of the PS foam. Taking only from the experimental data shown, it could be said that type and concentration of the inorganic substrates and also the physical form of the sample do not have pronounced influence on the chain reduction of the PS foam buried in the landfill site for a period of six months.

The statistical analysis was afforded to emphasis the above conclusion. In this section, two of the experimental parameters, type and amount of inorganic substrate added in the topsoil, were investigated. Each of these factors was investigated independently. The effect of physical form on the degradation of the foam has been previously described in the section 4.2.1 and there was no affect on the degradation rate. Only types and quantities of inorganic nitrate and sulfate would be discussed in this section.

Compare the molecular weight of the sample with equivalent concentration the nitrate and sulfate added into the topsoil, such as at 200 ppm, the results show that the molar mass reduction is similar. There seems to be no effect by the type of the inorganic substrate. By using the statistical value, *t*-test, as previously described by Eq. 4.1 - 4.6 with the level of significant(α) of 0.05, the statistical hypothesizes can be set as follow;

If H_o: $\bar{X} - \bar{Y} = 0$, it means that inorganic sulfate and nitrate does not have the effect on the degradation rate of the PS foam.

but if H_1: $\bar{X} - \bar{Y} \neq 0$, it means that inorganic sulfate and nitrate does have the effect on the degradation rate of the PS foam.

As explained in section 4.1.3, the statistical value of the *t*-test indicates that the null hypothesis, H_o, will be accepted if the calculated t from equation 4.4 falls into the range of $-t_{1-\alpha/2} < t < t_{1-\alpha/2}$. Vice versa, the H_o is rejected. From the statistical table of the probability distribution *t*-curve as shown in appendix C, for the α equal to 0.05 and the degree of freedom(ν) equal to 12, the $\pm t_{1-\alpha/2}$ are ±2.18. Table 4.4 shows the molecular weight of the PS foam obtained from the landfill experiments. By using these data, the calculated t value for a pair of data between nitrate and sulfate with equal concentration are summarized in Table 4.5. The results review that all the calculated t are felt between $\pm t_{1-\alpha/2}$, ±2.18. Therefore the H_0 for all cases are accepted. Accordingly, the conclusion could be stated that the families of the supplementary nutrition have no effect on the degradation of the PS foam when it was buried under the landfill.

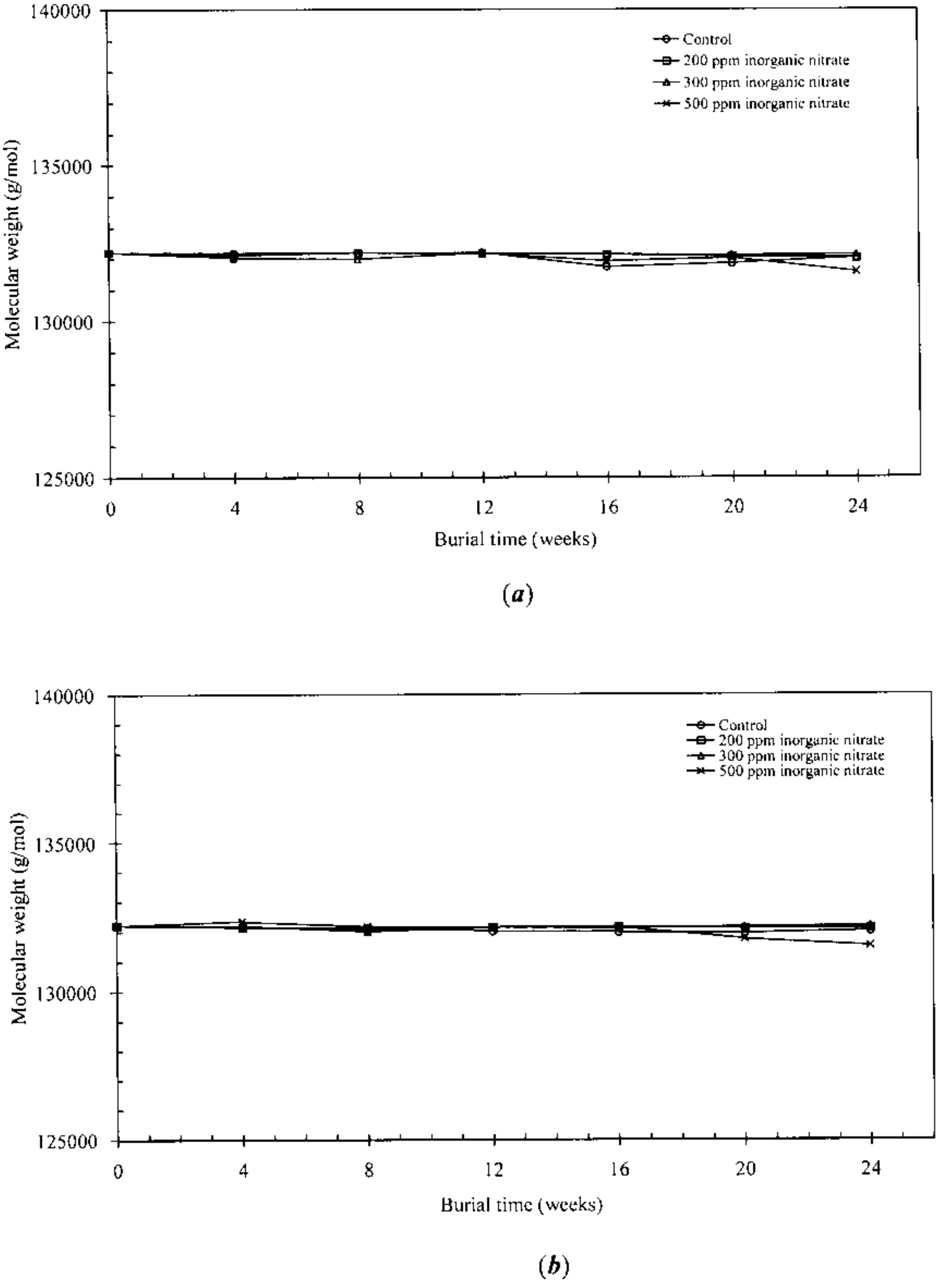
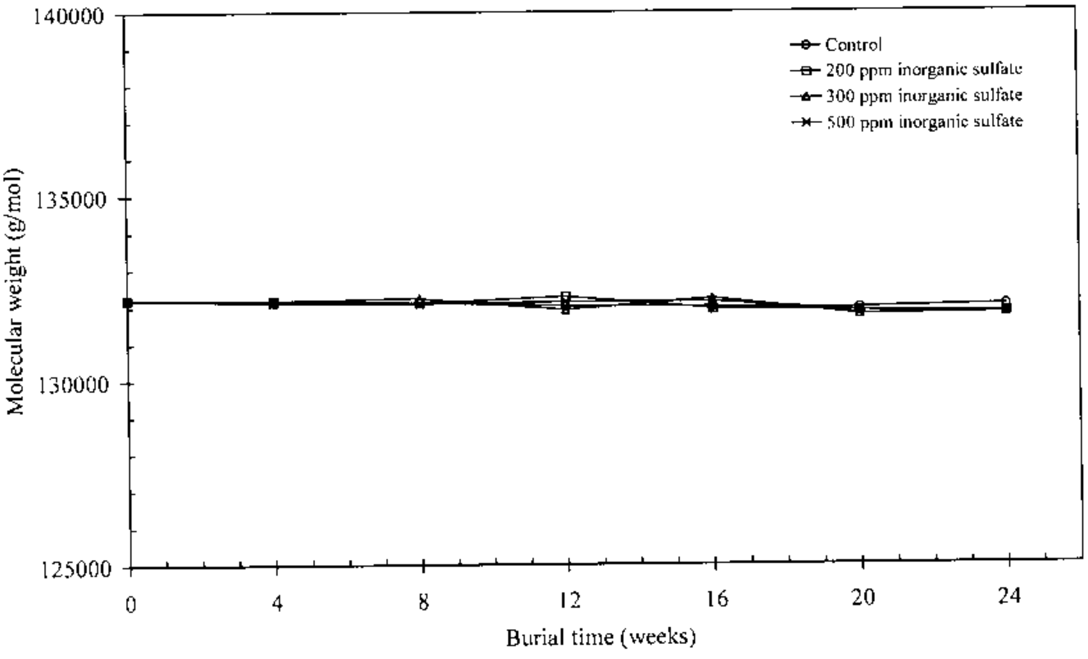
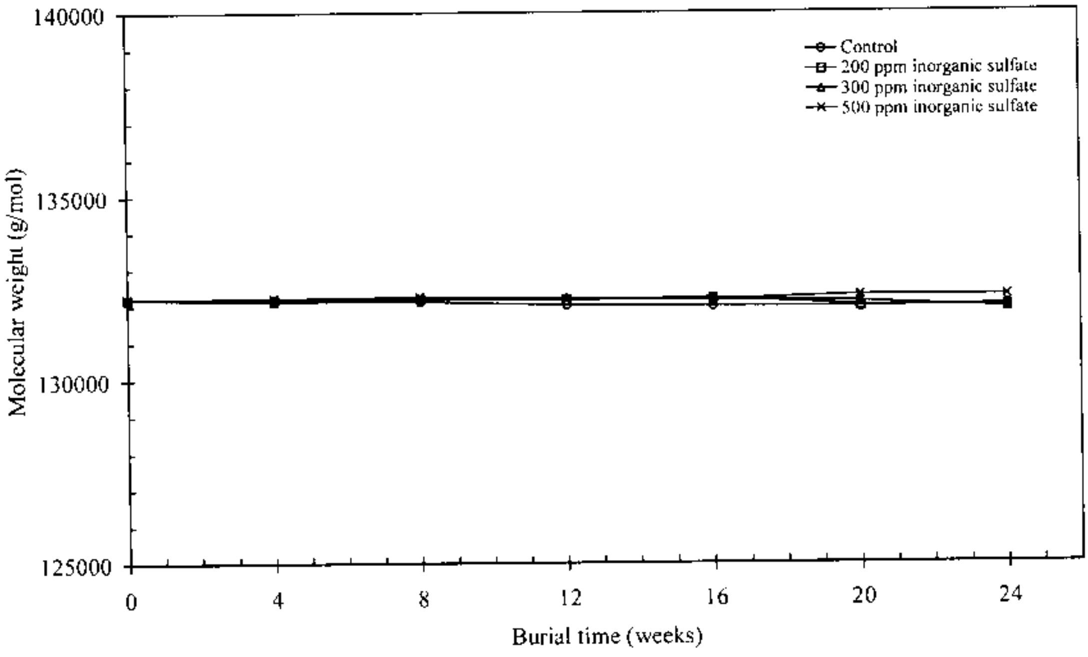


Figure 4.15 The variation of number average molecular weight of PS foam with the burial time under top soil doped with varied nitrate: (*a*) coarse crushed foam (*b*) fine crushed foam



(*a*)



(*b*)

Figure 4.16 The variation of number average molecular weight of PS foam with the burial time under top soil doped with varied sulfate: (***a***) coarse crushed foam (***b***) fine crushed foam

Table 4.4 Molecular weight of the foam obtained from landfill experiment

Burial time (weeks)	**Experimental condition**													
	Coarse crush foam + natural soil	Coarse crush foam + 200 ppm Nitrate	Coarse crush foam + 300 ppm Nitrate	Coarse crush foam + 500 ppm Nitrate	Coarse crush foam + 200 ppm Sulfate	Coarse crush foam + 300 ppm Sulfate	Coarse crush foam + 500 ppm Sulfate	Fine crush foam + natural soil	Fine crush foam + 200 ppm Nitrate	Fine crush foam + 300 ppm Nitrate	Fine crush foam + 500 ppm Nitrate	Fine crush foam + 200 ppm Sulfate	Fine crush foam + 300 ppm Sulfate	Fine crush foam + 500 ppm Sulfate
0	132210	132210	132210	132210	132210	132210	132210	132210	132210	132210	132210	132210	132210	132210
4	132195	132117	132023	132122	132191	132114	132218	132140	132152	132194	132334	132168	132162	132102
8	132185	132194	131984	132197	132186	132178	132244	132113	132103	132004	132175	132106	132229	132076
12	132198	132170	132183	132167	132143	132211	132167	132016	132167	132149	132141	132271	131906	132125
16	131729	132117	132138	131916	132207	132143	132125	131986	132160	132119	132142	131925	132212	132118
20	131836	132056	132105	131998	131989	132111	132278	131944	132119	132158	131753	131867	131759	131865
24	132016	132010	132111	131567	131953	131923	132259	132016	132111	132197	131533	131823	131789	131789
Mean	**132052**	**132124**	**132107**	**132025**	**132125**	**132127**	**132214**	**132060**	**132146**	**132147**	**132041**	**132052**	**132038**	**132040**
Variance	**39449**	**5354**	**6591**	**52626**	**11738**	**9807**	**2864**	**9085**	**1429**	**5006**	**82263**	**32014**	**44830**	**23495**

Table 4.5 Summary of the *t*-test of the coarse crushed foam samples buried in the landfill site with the inorganic nitrate and sulfate added into the topsoil

Concentration (ppm)	Average mean value($\overline{X}_i$, g/mol)		df (v)	The calculated *t*	The critical *t* ($t_{1-\alpha/2,\ v}$)	Conclusion
	Nitrate	Sulfate				
200	132124	132125	12	0.415	±2.18	H_0 Accepted
300	132107	132127	12	-0.410	±2.18	H_0 Accepted
500	132025	132214	12	-2.124	±2.18	H_0 Accepted

In order to investigate the dependency of the concentration of the inorganic substrate on the degradation rate of the PS foam, the single factor analysis of variance or one-way ANOVA method is employed. The basic principle of the analysis is to divide the variance of total data(SS_T) into two component parts namely variance between groups or treated variance(SS_{Tr}) and variance within groups or variance of error(SS_E), as shown in equation 4.19;

$$SS_T = SS_{Tr} + SS_E \tag{4.19}$$

Where SS_T = the variance of total data

SS_{Tr} = the summation of variance between groups or treated variance

SS_E = the summation of variance within groups or variance of error

The SS_{Tr} and SS_E are calculated by using the following equations;

$$SS_{T_r} = J\left[\sum_{i=1}^{I}\left(\overline{X}_i - \overline{X}_T\right)^2\right] \tag{4.20}$$

$$SS_E = \sum_{i=1}^{I} S_i^2 \tag{4.21}$$

$$\overline{X}_i = \frac{\sum_{j=1}^{J} x_{ij}}{J} \tag{4.22}$$

$$\overline{X}_T = \frac{\sum_{i=1}^{I} \overline{X}i}{I} \tag{4.23}$$

$$S_i^2 = \frac{\sum_{j=1}^{J} \left(x_{ij} - \overline{X}i\right)^2}{J - 1} \tag{4.24}$$

where J = A number of the data obtained in each groups of experiment

I = A number of experimental groups designed in this test

x_{ij}= the molecular weight data obtained from the experimental i^th^ group and the j^th^ observation count

$\overline{X}_i$ = mean value of the data obtained from the experimental i^th^ group

$\overline{X}_T$ = mean value of the overall data

From the results presented in Table 4.4, the series of the experimental data that can be classified by the concentration of the inorganic substrate into four groups, 0, 200, 300 and 500 ppm, respectively. Therefore, I equals to 4. Each group had 7 observed data and hence J equals to 7. So that, the test hypothesizes utilized in this study are;

H_0: $\overline{X}_1 = \overline{X}_2 = \overline{X}_3 = \overline{X}_4$, it means that the degradation of the PS foam does not depend on the concentration of the inorganic supplementary nutrition

and H_1: $\overline{X}_i \neq \overline{X}_j$ for any i and j it means that the degradation of the PS foam does depend on the concentration of the inorganic supplementary nutrition

The statistical f-test could also be used for verifying the level of confidence regarding to the H_0 acceptation. The value of the f can be calculated by using equation 4.25. The calculated one would be compared with the critical value ($f_{1-\alpha, v1, v2}$ or $f_{critical}$)

that is shown in the statistical table of the f distribution in appendix C. If the calculated $f < f_{\text{critical}}$, then the H_0 is accepted. Vice versa, the H_0 would be rejected.

$$f = \frac{MS_{Tr}}{MS_E} \tag{4.25}$$

$$\text{Mean square}(MS_{Tr}) = \frac{SS_{Tr}}{\nu_1} \tag{4.26}$$

$$\text{Mean square}(MS_E) = \frac{SS_E}{\nu_2} \tag{4.27}$$

Where ν_1 = degree of freedom of $SS_{Tr} = I - 1$

and ν_2 = degree of freedom of $SS_E = IJ - I$

In this study, the level of significant for accepts H_0 is set at 0.05. The calculated f value of the experimental data obtained by using the equation 4.20 to 4.27 are shown in table 4.6.

Table 4.6 ANOVA table of the coarse crushed foam sample buried under the topsoil in which the amount of inorganic nitrate varied from 0 to 500 ppm

Source of Variation	**Sum of square**	**Degree of Freedom**	**Mean Square**	Calculated f	Critical f
Between Groups	45473.28	I-1 = 3	15157.76	0.58	3.01
Within Groups	624123.14	$IJ - I$ = 24	26005.13		
Total	669596.42	IJ – 1 = 27			

From the ANOVA table, it reviews that the calculated f is 0.58 and the critical f value, obtained from the statistical table in Appendix C, is 3.01. The calculated f is less than the critical value. It means that the H_0 is accepted. From the result of the test, it is reinforced that the degradation of the PS foam, with in 6 months period, does not depend on the concentration of the inorganic supplementary nutrition

From all of the above outcome, it could be confidently concluded that the physical form of the foam sample, family and also concentration inorganic substrate in the landfill topsoil do not effected on the degradation reaction within the 6 months period.

4.3 Water Incubation Conditions

This experiment was set to adopt the condition where the foam would be disposed into water resources and eventually reached to the seashore. The experiment was performed by soaking the samples in seawater and wastewater for a period of 6 months. The effect of surface area, by mean of coarse and fine crushed, on the degradation rate of the samples was also investigated. Two experimental environments, open and the oxygen limited atmospheric where they were called *open* and *closed* systems in this study, were applied. If the polymer chain were simultaneously broken down, the degraded product would be dissolved or suspended into the liquid phase, and hence the quality of the soaking water, COD, would be changed. The details of experiment were described earlier in Chapter III.

4.3.1 Effect of Surface Area

When the coarse and fine crushed PS foam samples was soaked in the seawater and wastewater for a period of 6 months, decreasing in the molecular mass with the incubation time are illustrated in Figure 4.17 and 4.18, respectively. Figure 4.17 shows that molar masses of the foam soaked in seawater under the open and close system were slowly depleted with the incubation time. It started from 132,000 g/mol to approximately 115,000 g/mol at the incubation time of 6 months for all the samples. The plot seems to review that the decreasing in the chain length are regardless to the physical form of the sample and also the test conditions. The similar trends were also observed for the result obtained in the wastewater as shown in Figure 4.18. Taking only this observation, it would lead to the conclusion that the surface areas, the differences in soaking waters and the concentration of oxygen do not have any significantly effect on the degradation rate of the PS foam. In the order to reinforce the above judgement, the statistical *t*-test, as described in Eq. 4.1 - 4.6, with

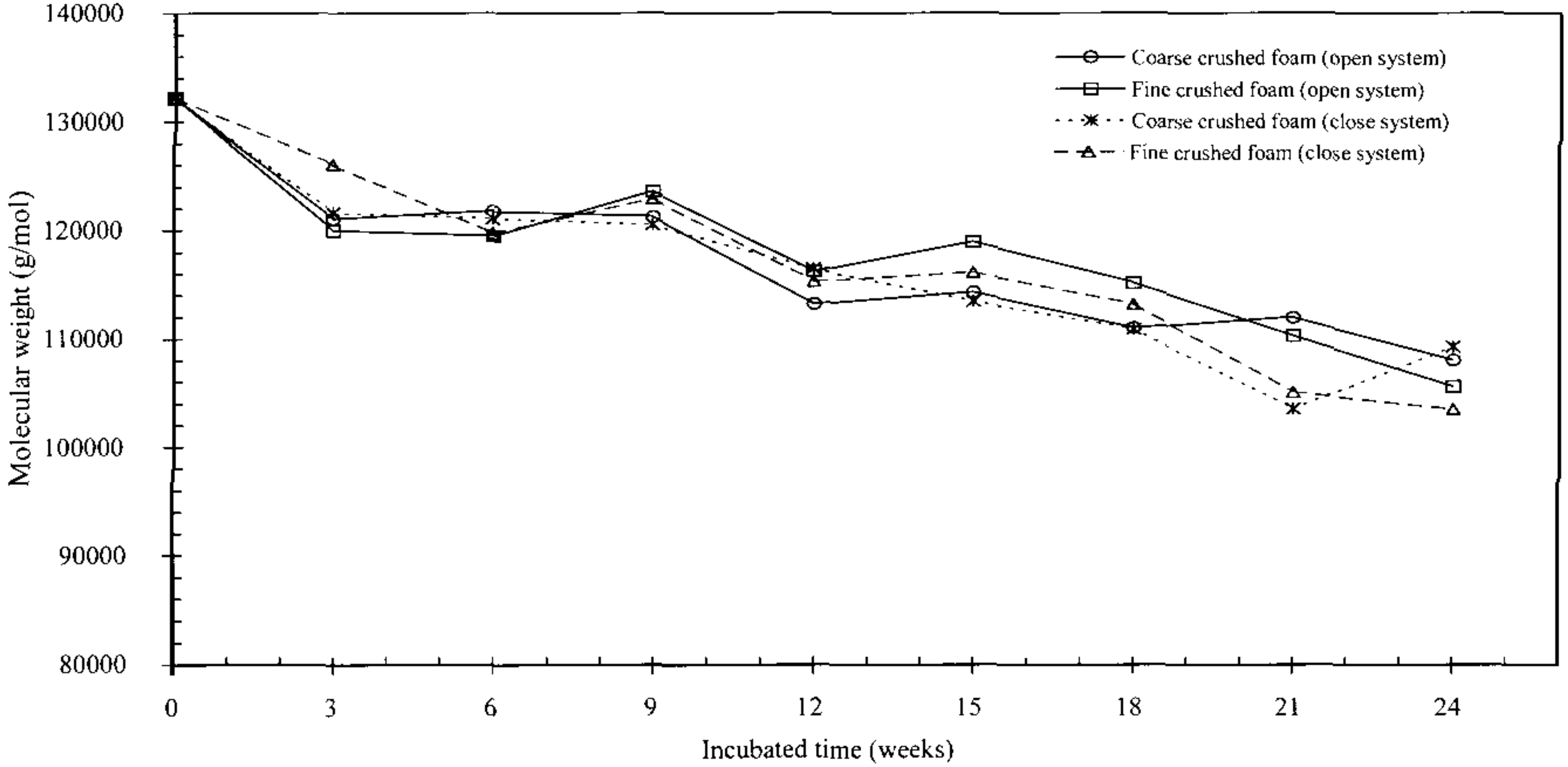


Figure 4.17 *The variation of number average molecular weight of PS foam with the soaking time in seawater*

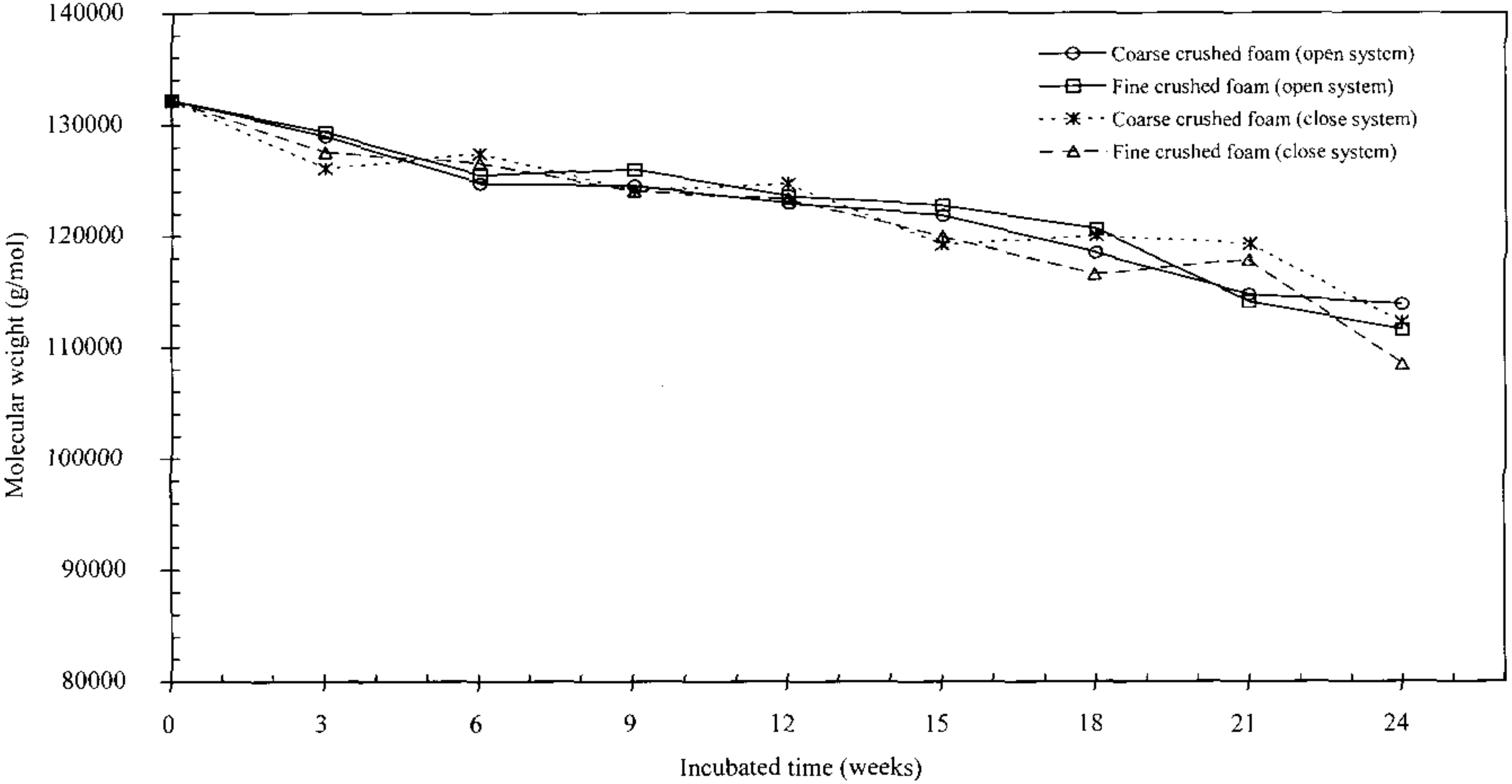


Figure 4.18 The variation of number average molecular weight of PS foam with the soaking time in wastewater

the level of significant(α) of 0.05 was employed to verify the difference in average mean value of the results obtained in this experiment. The testing parameters are physical form of the foam, type of soaking water and the incubated system. The statistical hypothesizes for the test are;

If $H_o: \overline{X} - \overline{Y} = 0$, it means that the pair of the data obtained from different test conditions are identical,

but if $H_1: \overline{X} - \overline{Y} \neq 0$, it means that the pair of the data obtained from different test conditions are unlike and it depends on tested parameters.

From the statistical t- test, the Null hypothesis, H_o, would be accepted if the calculated t from equation 4.4 falls in between $- t_{1-\alpha/2} < t < t_{1-\alpha/2}$. Vice versa, the H_o is rejected. In this study, the 9 data points were observed for each group regarding to the incubated time as shown in Figure 4.17 and 4.18. Therefore, the degree of freedom(ν) used in the calculation were 16 and the critical t value, $t_{1-\alpha/2}$, that obtained from the referee table was 1.746. Table 4.7 - 4.9 summarize the value of t-test obtained from various incubation conditions. The figures review that all the calculated t values are felt in between $- t_{1-\alpha/2} < t < t_{1-\alpha/2}$ for all cases. Consequently, the H_0 is accepted for any pair of testing parameters. It means that the physical form of the foam sample, varying of the incubated system and also differences in the incubating water, seawater and wastewater, do not have any affect on the degradation rate of the foam within a 6 months period.

From these outcomes, they would suggest that the degradation process of the PS foam in water is very slow. The microorganism existed in the seawater and wastewater would not use the sample as a carbon source. However, the chain of the sample was slowly broken down in the soaking waters caused by the photoreaction similarly to those found in open-air exposure. But, the degradation rate in the water is more slowly than when in directly expose to the sunlight. It can be explained that the water acts as the screen to absorb large amount of energy from the sunlight. Only slightly fraction of radiation that is reached to the foam sample and degrading the polymer chain.

Table 4.7 Summary of the *t*-test values regarding to the physical form of the foam when soaked in seawater and wastewater under close and open systems

Soaking Condition	System	Average mean value		df (v)	Calculated t	Critical t ($t_{1-\alpha/2,\ v}$)	Conclusion
		Coarse crushed	Fine crushed				
Sea water	Open	117268.4	117966.3	16	-0.21	± 1.746	***Ho*** accepted
	Close	116564.1	117122.7	16	-0.133	± 1.746	***Ho*** accepted
Waste water	open	122476.6	122846.9	16	-0.123	± 1.746	***Ho*** accepted
	Close	122133.8	119118.9	16	1.154	± 1.746	***Ho*** accepted

Table 4.8 Summary of the *t*-test values regarding the incubation system, open and close

Sample	Physical form	Average mean value		df (v)	The calculated t	The critical t ($t_{1-\alpha/2,\ v}$)	Conclusion
		Open system	Close system				
Sea water	Coarse	117218.4	116564.1	16	0.174	±1.746	***Ho*** accepted
	Fine	117966.3	117122.7	16	0.210	±1.746	***Ho*** accepted
Waste water	Coarse	122476.6	121022.7	16	0.529	±1.746	***Ho*** accepted
	Fine	122846.9	119118.9	16	1.206	±1.746	***Ho*** accepted

Table 4.9 Summary of the *t*-test values regarding to the differences in the incubated waters

Physical form	System	Average mean value		df (v)	The calculated t	The critical t ($t_{1-\alpha/2,\ v}$)	Conclusion
		Seawater	Wastewater				
Coarse crushed	Open	117218.4	122476.6	16	-1.630	±1.746	***Ho*** accepted
	Close	116504.1	121022.7	16	-1.322	±1.746	***Ho*** accepted
Fine crushed	Open	117966.3	122846.9	16	-1.446	±1.746	***Ho*** accepted
	Close	117122.7	119118.9	16	-0.527	±1.746	***Ho*** accepted

4.3.2 Quality of Incubated Waters

When the polymer chains of foam sample were simultaneously broken down into smaller molecules, the degraded product would be dissolved in soaking liquid. Consequently, the quality of the soaking water by mean of COD would be increased. In this study, the COD of the soaking water was measured as a function of incubation time.

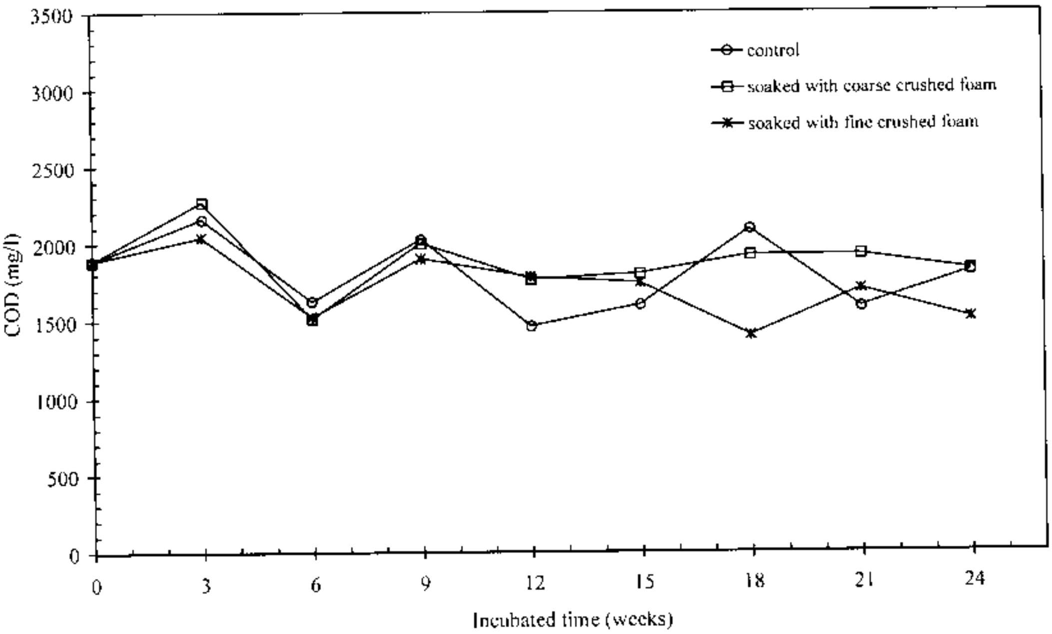
Figure 4.19(*a*) and Figure 4.19(*b*) show the relationship between COD of the seawater and incubation time for a period of 6 months in the open and close system, respectively. The coarse and fine crushed samples were used for investigation. Surprisingly, from Figure 4.19(*a*), the plot shows that the COD are approximately constant at 1880 mg/l with the incubation time for all cases. The similar result is also observed in the close system as seen in Figure 4.19(*b*). From the data found it would suggest that the degraded products does not dissolve in seawater. Thus, the quality of the soaking water was not changed.

By using the statistical method, one way ANOVA, to determine the difference in the COD value of the water samples of all cases and using the statistical *t* test to investigate the difference of the COD of the incubated water between the systems, open and close. The ANOVA test hypothesizes are;

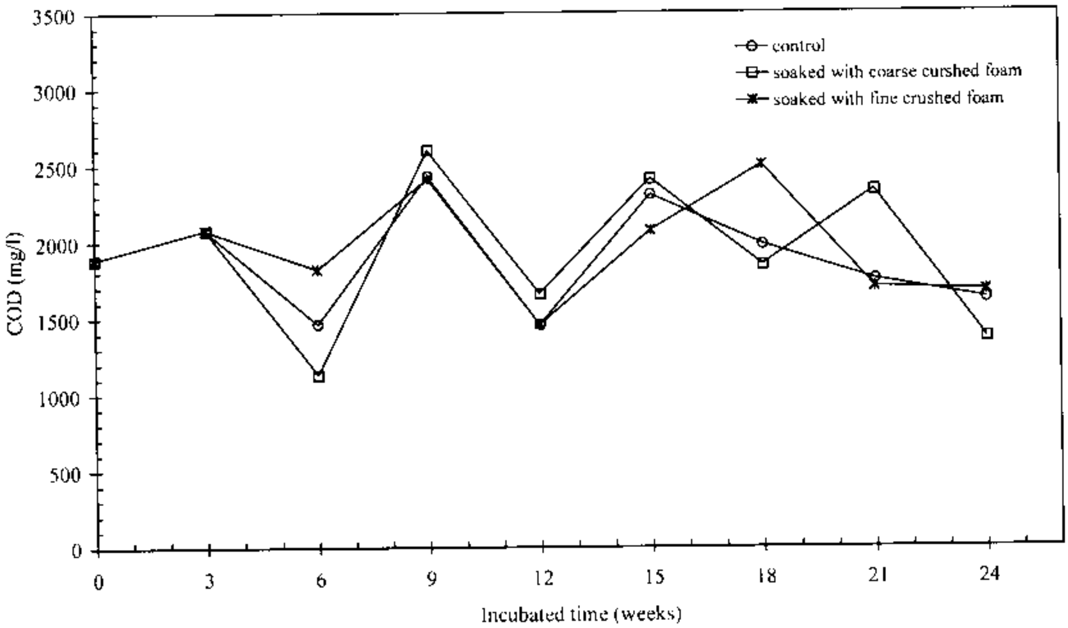
If H_0: $\overline{X}_1 = \overline{X}_2 = \overline{X}_3$, *it means that there is no changing in* COD of the water sample for all cases.

and if H_1: $\overline{X}_i \neq \overline{X}_j$ for any i and j it means that the COD of the water sample are depended on the incubation time.

When the level of significant to accept H_0 is set at 0.05. The *f* value of the test can be calculated by using the equation 4.25 - 4.27. There are three groups of experiment regarding to control, coarse and fine crushed, respectively. Therefore, the I is equal to 3. In each group, there are nine data points measured. Hence, the J is



(*a*)



(*b*)

Figure 4.19 The COD of seawater: (*a*) open system (*b*) close system equal to 9. Table 4.10 and 4.11 summarize the ANOVA table for the experimental data obtained from open and close system, respectively.

Table 4.10 ANOVA table of the seawater under the open system

Source of Variation	**Sum of square**	**Degree of freedom**	**Mean Square**	Calculated f	Critical f
Between Groups	166266.7	I-1 = 2	83133.4	1.581	3.40
Within Groups	1262211.6	$IJ - I = 24$	52592.1		
Total	*1428478.3*	$IJ - 1 = 26$			

Table 4.11 ANOVA table of the seawater under the close system

Source of Variation	**Sum of square**	**Degree of freedom**	**Mean Square**	Calculated f	Critical f
Between Groups	89902.5	I-1 = 2	44951.3	0.322	3.40
Within Groups	3350136.2	$IJ - I = 24$	139589.0		
Total	3440038.7	$IJ - 1 = 26$			

From the ANOVA table, it reviews that the calculated f for open and close system are 1.581 and 0.322, respectively, and the critical f value, obtained from the statistical table in Appendix C, for the test is 3.40. In comparison, the calculated f is *less than the critical value. Consequently, the* H_0 *is accepted.* The ANOVA test indicates that there is no changing in COD of the incubated water sample for all cases. It means that there was no degraded products dissolved into water.

In the order to differentiate the changing of COD of the soaked water between two incubation conditions, the statistical t-test with the level of significant(α) of 0.05 and the degree of freedom of 16 was adopted. Again, the statistical hypothesizes are;

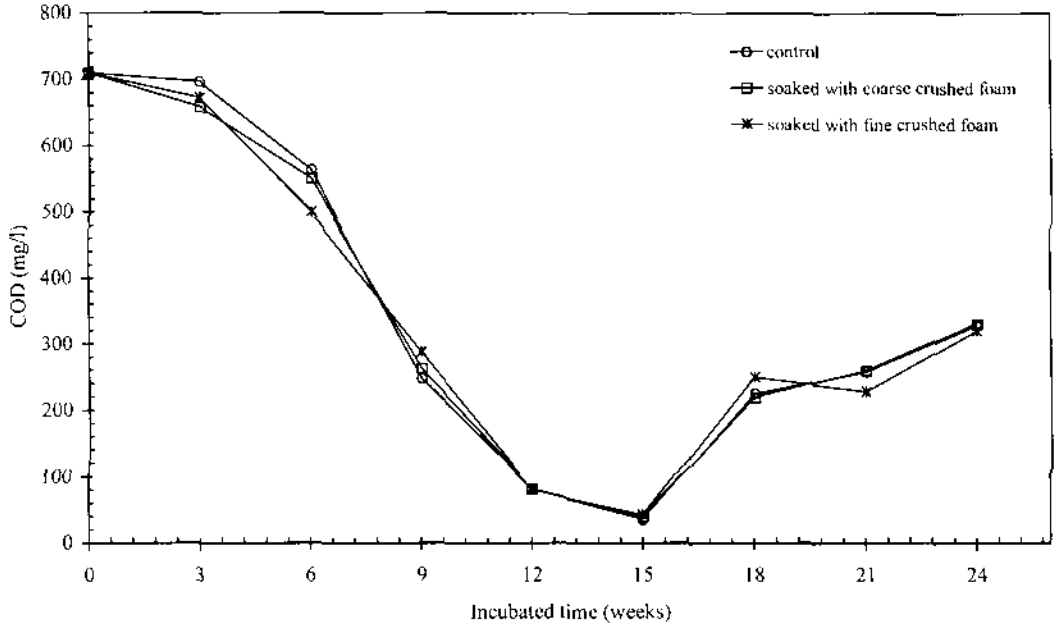
If $H_0: \bar{X} - \bar{Y} = 0$, it means that changing in COD of soaked water does not depend on the incubation conditions, but if $H_1: \overline{X} - \overline{Y} \neq 0$, it means that changing in COD of soaked water does depend on the incubation conditions

From COD data obtained, the calculated t value for all cases can be determined and summarized in Table 4.12. The calculated t values obtained from all testing condition are felt within the critical t. Therefore, the H_o are accepted. It means that changing in COD of the soaked water does not depend on the incubation conditions.

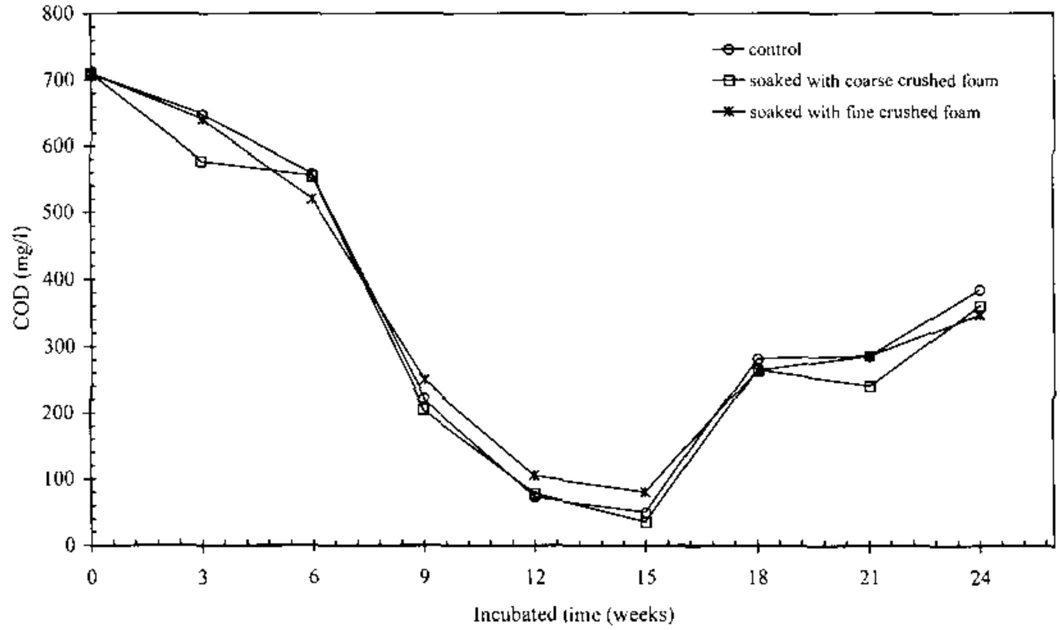
Table 4.12 Summary of the *t*-test of the COD for soaked seawater samples in close and open system

Water Samples	Average mean value of COD ($\overline{X}_i$, mg/l)		df (v)	The calculated t	The critical t ($t_{1-\alpha/2,\ v}$)	Conclusion
	Open system	Close system				
Control	1803.3	1877.2	16	-0.687	±1.746	H_0 Accepted
Soaked with coarse crushed foam	1813.2	1877.2	16	0.409	±1.746	H_0 Accepted
Soaked with fine crushed foam	1778.6	1955.6	16	-1.365	±1.746	H_0 Accepted

Figure 4.20(*a*) and Figure 4.20(*b*) shows variation of COD value of the wastewater with the soaking time in the open and close system, respectively. As seen from the plot that the COD were gradually decreased from 730 mg/l to approximately 50 mg/l for a period of the first 15 weeks. After that, it was slowly increased and eventually reach to 300 mg/l in the last 24th week. The similar trends were also observed for the close system.



(*a*)



(*b*)

Figure 4.20 The COD of wastewater: (*a*) open system (*b*) close system

If the foam samples were gradually degraded when they were soaked in the wastewater, the degrade-product would pollute the soaking water. Consequently, the COD of the water would be increased. Contradictorily, the results show that the COD of the waters were not increased with incubation time. From the graphs, they could be explained that the initial reduction of the COD was caused by a self-purification of the wastewater by the microbes that degrade the waste materials in the water [Metcalf & Eddy (1991)]. Also, the photosynthesis process by the algae was evidence and quickly propagated. Finally, the eutrophication was occurred. This condition will cause in the rising of COD. Subsequently, the conclusion could be suggested that the degrade-products of the polymer chain were not dissolved in the water and contributed to the COD value of the incubated water. It might be true when only small amounts of chain are degraded.

In order to confirm the previous conclusion, the statistical method, one way ANOVA was applied to differentiate the variation of the COD of water sample. The *ANOVA test hypothesizes are;*

H_0: $\bar{X}_1 = \bar{X}_2 = \bar{X}_3$, it means that variation of COD in the wastewater samples do not depend on the PS foam degradation,

H_1: $\bar{X}_i \neq \bar{X}_j$ for any i and j it means that variation of COD in the wastewater samples depend on the PS foam degradation.

In this study, if the 95% degree of confidence is used, in the other words the level of significance used in the test is 0.05. The calculated f values were also derived by using the equation 4.25 to 4.27 and they are summarized in Table 4.13 and 4.14 for the open and close system, respectively.

Table 4.13 ANOVA table of the wastewater under the open system

Source of Variation	**Sum of square**	**Degree of Freedom**	**Mean Square**	Calculated *f*	Critical *f*
Between Groups	169.6	I-1 = 2	84.8	0.001	3.40
Within Groups	1421173.1	$IJ - I = 24$	59215.5		
Total	1421342.7	$IJ - 1 = 26$			

Table 4.14 ANOVA table of the seawater under the close system

Source of Variation	**Sum of square**	**Degree of Freedom**	**Mean Square**	Calculated *f*	Critical *f*
Between Groups	3000.7	I-1 = 2	1500.3	0.028	3.40
Within Groups	1276659.3	$IJ - I = 24$	53194.1		
Total	1279660.0	$IJ - 1 = 26$			

From the ANOVA tables, it shows that the calculated f values for open and close system are 0.001 and 0.028, respectively. The critical f value, obtained from the statistical table in Appendix C, for these tests is 3.40. It is obviously seen that the calculated f is less than the critical value. Therefore, the H_0 is accepted. From the conclusion of the statistical testing, it indicates that variation of COD in the wastewater are not caused by the degradation process of the PS foam for both in the open and close soaking conditions.

From both of the results obtained directly from the actual experiment and also from the statistical testing, it can be pronounced that the PS foam is hardly degraded when buried in landfill or disposed into water resources. Photodegradation is the only existing method *that the foam sample can be rapidly degraded. From this research* work, a clear conclusion can be made that the degradation reaction of the PS foam can not be enhanced by the biodegradation reaction. It can be quickly decomposed by the photo degradation and the accelerators can be applied to speed up the reaction.

CHAPTER V
CONCLUSIONS

The main aim of this research work was to investigate the degradation phenomenon of the PS foam in the conditions imitated to the actual exposure environment. They were natural light exposure, landfill, and the water incubated conditions. The effects of photo-accelerators, Benzoyl peroxide and AIBN, physical form of the foam sample, and concentration of the inorganic supplementary nutrition, nitrate, and sulfate in the topsoil, on degradation rate of the PS foam were investigated. The possibility of applying the experimental data from the standard weatherometer to directly forecast the degradation of the PS foam in the real natural environment was also studied. The experimental data were investigated for a period of six months. The degradation rate was monitored by using the molecular weight reduction that was characterized by GPC.

When the PS foam was exposed under the natural sunlight, the decomposition by the photoreaction rapidly occurred. The degradation mechanism of this polymer was a chain scission process. The decomposition time was linearly corresponded to and depended on the molecular weight of the starting feedstock. The higher molecular weight of the foam, the longer time was needed in the order to break down the samples into pieces and eventually fall apart. The degradation time of this solid waste was less than 6 months. The deterioration time was shorten when the samples were subjected to external force such as strong wind and heavy rainfall. By using the mathematical model, it was preliminarily observed that the degradation reaction of the PS foam increased when the peroxide accelerator was incorporated onto the surface of the sample.

In the accelerated condition, using the standard weatherometer chamber, the specimens were exposed to the artificial atmosphere, which was simulated closely to the actual open atmosphere except the test tempePrature as described in section 3.4.3. Effects of the accelerator concentrations were also determined. It was observed that the data from the accelerated chamber was identical to those obtained from effects caused by natural causes; and the accelerated chamber could be directly applied to predict the degradation of PS foam in natural environment. The experimental and the statistical calculation results obtained from the chamber experiment also illustrated that degradation rate of this foam was influenced by the peroxide and AIBN accelerators. These accelerators could generate more highly reactive radical species by the photolysis and they would be attracted on the PS chain. Subsequently, the polymer molecule would either be broken down or form the active site on the chain backbone and eventually underwent chain shortening. The experimental results also indicated that degradation rate depends on the quantity of the accelerator used. The AIBN accelerator had stronger influence on the degradation of the PS foam than the Benzoyl peroxide.

When the coarse and fine crushed PS foam were buried under the landfill soil having different in nitrate and sulfate concentration, it was found that molecular weight of the foam could not be decreased within six months burial time. It was possible to make a strong conclusion that increasing in the surface area of the foam and the concentration of the supplementary nutrition did not have a significantly effect on the degradation rate of this polymer.

To imitate the degradation of the PS foam when it was dumped in water bodies, the coarse and fine crushed PS foam were soaked into the seawater and wastewater. The experimental results illustrated that the foam were slowly degraded within six months time and the degraded products did not influenced the quality, COD, of the water. The outcome also pointed out that the increasing in surface area did not have any influence on the degradation of this polymer.

From this research work, it could be pronounced that within six months periods, the PS foam was hardly degraded when buried in the landfill and disposed into the water resources. Photodegradation was the only existing mechanism that the foam could be rapidly degraded and the accelerators could be applied to speed up the reaction. The obvious conclusion might be made that the degradation reaction of the PS foam was not caused by the biodegradation reaction.

Recommendation For Further Work

The study in degradation of plastics waste for example Polyethylene or Poly (ethylene terephthalate), PET, in the natural environment are the interesting issues. The result form the study could be used as the basic information for solid waste management. The study of plastic degradation should be further studied in the aspect of:

(i) The degradation of the other main polymer in the municipal solid waste(MSW)
(ii) The effect of other types of the photo accelerators might be investigated
(iii) The optimum concentration of photo accelerator used to accelerate the degradation rate of the plastic must be obtained.
(iv) The degradation of the PS foam in the long time period, longer than six months, must be observed.

Research Publication

Parts of this work were published and are being presented in the following conferences;

Kenharaj, R., Meekum, U. and Polprasert, C. (2000). Environmental aspect of the Polystyrene foam degradation. In **The first Thailand material science and technology conference 2000** (pp 401-403). MTEC. Bangkok, Thailand.

Meekum, U., Kenharaj, R. and Polprasert, C. (2000). Environmental aspect of the polystyrene foam degradation. In **The 10th Annual Meeting of Thailand Chemical engineering and applied chemistry** (pp 125-132). Mahanakhorn University of Technology. Bangkok, Thailand.

Meekum, U., Kenharaj, R. and Polprasert, C. (2001). Environmental engineering approach in Polystyrene foam degradation. In **International symposium on green chemistry** (p IL5). IUPAC. Delhi, India.

Meekum, U. (submitted). Comparative study of Polystyrene foam degradation in the open-air and artificial weathering exposure. In **ANTEC 2002**. Society of Plastic Engineering. San-Francisco, USA

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APPENDIX A

Calculation for Converts Natural Exposure Time to Xenon Arc Lamp Weatherometer Time

The calculation to convert the natural exposure time to the Xenon arc lamp weatherometer equivalent time.

Calculation concept:

The concept of converting the natural exposure time to the weatherometer time is, the dosing of energy that produced from the weatherometer to the specimen must be equaled to the energy that the sample was received from the natural sunlight.

Meteorological data:

The total solar radiation in one year exposure (from Table 3.2) = 5058.0 MJ/m^2.

The UV energy (λ< 295 nm) that could be damaged the plastic was about 5 % of the solar radiation obtained [Mustafa (1993)].

Therefore, total UV energy obtained from the Solar radiation = 252.9 MJ/m^2.

Weatherometer data:

From the instrument specification;

For the Boro-Borosilicate inner filter, the factor to convert the total natural UV energy to the equivalent energy at λ = 340 nm = 0.01025

The UV energy (@340 nm) produced by using the weatherometer at 0.5 W/ m^2 irradiation setting = 1.8 kJ/m^2-hour

Calculation:

From the data above, to convert the open air exposure time to the weatherometer time, the total UV energy @ 340 nm dosage per year are divided by the value of energy produced by the weatherometer as show follow.

$$\text{Weatherometer time} = \frac{\text{The natural UV energy dosage per year} \ \ \text{X} \ \ 0.01025}{\text{The UV energy produce by weatheromder}}$$

$$= \frac{252.9 \;\; \text{MJ/m}^2 \;\; \text{X} \;\; 0.01025}{1.8 \;\; \text{kJ/m}^2 \text{ - hour}}$$

$$= 1440 \text{ hours}$$

So, one year in natural exposure correspond to **1440 hours** in the weatherometer.

APPENDIX B

Statistical Analysis Results

Statistical Analysis by Using SPSS Program

B1 Linear regression analysis

Table B1 One way ANOVA table for linear regression of neat PS foam sample in natural exposure condition [b]

Model	Sum of square	df	Mean square	*f*	Sig.
Regression	1.012	1	1.012	6.556	0.026[a]
Residual	1.699	11	0.154		
Total	2.711	12			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B2 The linear regression Coefficients of neat PS foam sample in natural exposure condition [b]

Model	Unstandardized Coefficients		Standardized Coefficients	*t*	Sig.
	B	Std. Error	Beta		
(constant)	-3.455	1.640		-2.107	0.024
LOGXN	1.577	0.616	0.611	2.560	0.024

a. Dependent Variable: LOGRATE

Table B3 One way ANOVA table of 1% Benzoyl peroxide coated PS foam sample in natural exposure condition [b]

Model	Sum of square	df	Mean square	*f*	Sig.
Regression	2.786	1	2.768	20.999	0.000[a]
Residual	1.858	14	0.133		
Total	4.644	15			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B4 The linear regression Coefficients of 1% Benzoyl peroxide coated PS foam sample in natural exposure condition [b]

Model	Unstandardized Coefficients		Standardized Coefficients	*t*	Sig.
	B	Std. Error	Beta		
(constant)	-3.894	0.958		-4.066	0.001[a]
LOGXN	1.746	0.381	0.775	4.582	0.000[a]

a. Dependent Variable: LOGRATE

Table B5 One way ANOVA table of neat PS foam sample in accelerated condition [b]

Model	Sum of square	df	Mean square	*f*	Sig.
Regression	1.019	1	1.019	252.540	0.001[a]
Residual	0.0012	3	4.036e-3		
Total	1.031	4			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B6 The linear regression Coefficients of neat PS foam sample in accelerated condition[b]

Model	**Unstandardized Coefficients**		**Standardized Coefficients**	*t*	**Sig.**
	B	Std. Error	Beta		
(constant)	-4.706	0.297		-15.826	0.001
LOGXN	1.776	0.112	0.994	14.892	0.001

a. Dependent Variable: LOGRATE

Table B7 One way ANOVA table of 1% Benzoyl peroxide coated PS foam sample in accelerated condition[b]

Model	**Sum of square**	**df**	**Mean square**	*f*	**Sig.**
Regression	3.204	1	3.204	12.024	0.010[a]
Residual	1.866	7	0.267		
Total	5.070	8			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B8 The linear regression Coefficients of 1% Benzoyl peroxide coated PS foam sample in accelerated condition[b]

Model	**Unstandardized Coefficients**		**Standardized Coefficients**	*t*	**Sig.**
	B	Std. Error	Beta		
(constant)	-4.742	1.283		-3.696	0.008
LOGXN	1.823	0.526	0.795	3.468	0.010

a. Dependent Variable: LOGRATE

Table B9 One way ANOVA table of 2% Benzoyl peroxide coated PS foam sample in accelerated condition [b]

Model	**Sum of square**	**df**	**Mean square**	***f***	**Sig.**
Regression	1.984	1	1.984	34.969	0.001[a]
Residual	0.340	6	5.675e-2		
Total	2.325	7			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B10 The linear regression Coefficients of 2% Benzoyl peroxide coated PS foam sample in accelerated condition [b]

Model	**Unstandardized Coefficients**		**Standardized Coefficients**	***t***	**Sig.**
	B	Std. Error	Beta		
(constant)	-5.048	0.814		-6.199	0.001
LOGXN	1.912	0.323	0.924	5.913	0.001

a. Dependent Variable: LOGRATE

Table B11 One way ANOVA table of 3% Benzoyl peroxide coated PS foam sample in accelerated condition [b]

Model	**Sum of square**	**df**	**Mean square**	***f***	**Sig.**
Regression	1.614	1	1.164	229.989	0.001[a]
Residual	1.518e-2	3	5.061e-3		
Total	1.179	4			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B12 The linear regression Coefficients of 3% Benzoyl peroxide coated PS foam sample in accelerated condition [b]

Model	Unstandardized Coefficients		Standardized Coefficients	*t*	Sig.
	B	Std. Error	Beta		
(constant)	-5.157	0.339		-15.222	0.001
LOGXN	1.952	0.129	0.994	15.165	0.001

a. Dependent Variable: LOGRATE

Table B13 One way ANOVA table of 1% AIBN coated PS foam sample in accelerated condition [b]

Model	Sum of square	df	Mean square	*f*	Sig.
Regression	3.241	1	3.241	282.524	0.000[a]
Residual	6.883e-2	6	1.147e-2		
Total	3.310	7			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B14 The linear regression Coefficients of 1% AIBN coated PS foam sample in accelerated condition [b]

Model	Unstandardized Coefficients		Standardized Coefficients	*t*	Sig.
	B	Std. Error	Beta		
(constant)	-5.078	0.278		-18.276	0.000
LOGXN	1.964	0.117	0.990	16.808	0.000

a. Dependent Variable: LOGRATE

Table B15 One way ANOVA table of 2% AIBN coated PS foam sample in accelerated condition [b]

Model	**Sum of square**	**df**	**Mean square**	***f***	**Sig.**
Regression	3.162	1	3.162	41.632	0.001[a]
Residual	0.456	6	7.596e-2		
Total	3.618	7			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B16 The linear regression Coefficients of 2% AIBN coated PS foam sample in accelerated condition [b]

Model	**Unstandardized Coefficients**		**Standardized Coefficients**	***t***	**Sig.**
	B	Std. Error	Beta		
(constant)	-5.206	0.751		-6.930	0.000
LOGXN	2.016	0.313	0.935	6.452	0.001

a. Dependent Variable: LOGRATE

Table B17 One way ANOVA table of 3% AIBN coated PS foam sample in accelerated condition [b]

Model	**Sum of square**	**df**	**Mean square**	***f***	**Sig.**
Regression	2.700	1	2.700	11.351	0.020[a]
Residual	1.189	5	0.238		
Total	3.889	6			

a. Predictor: (constant),LOGXN

b. Dependent variable: LOGRATE

Table B18 The linear regression Coefficients of 3% AIBN coated PS foam sample in accelerated condition [b]

Model	Unstandardized Coefficients		Standardized Coefficients	*t*	Sig.
	B	Std. Error	Beta		
(constant)	-5.749	1.570		-3.662	0.015
LOGXN	2.275	0.675	0.833	3.369	0.020

a. Dependent Variable: LOGRATE

B2 Correlation analysis

Table B19 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of neat PS foam sample in the natural exposure condition

		Experiment	Model
Experiment	Pearson Correlation	1.00	0.950
	Sig.(2-Tailed)	-	0.000
	N	22	22
Model	Pearson Correlation	0.950	1.00
	Sig.(2-Tailed)	0.000	-
	N	22	22

Table B20 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 1% Benzoyl peroxide coated PS foam sample in the natural exposure condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.938
	Sig.(2-Tailed)	-	0.000
	N	22	22
Model	Pearson Correlation	0.938	1.00
	Sig.(2-Tailed)	0.000	-
	N	22	22

Table B21 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of neat PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.997
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.997	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B22 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 1% Benzoyl peroxide coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.995
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.995	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B23 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 2% Benzoyl peroxide coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.998
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.998	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B24 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 3% Benzoyl peroxide coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.998
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.998	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B25 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 1% AIBN coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.997
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.997	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B26 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 2% AIBN coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.997
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.997	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

Table B27 The correlation coefficient analysis of the $\overline{X}_n$ obtained from the model calculation and the experiment of 3% AIBN coated PS foam sample accelerated condition

		Experiment	**Model**
Experiment	Pearson Correlation	1.00	0.995
	Sig.(2-Tailed)	-	0.000
	N	13	13
Model	Pearson Correlation	0.995	1.00
	Sig.(2-Tailed)	0.000	-
	N	13	13

B3 Mean comparison analysis

Table 28 Independent sample *t*-test of the Uncoated PS foam between the natural exposure and the accelerated condition

Sample	**Average mean value**		**df**	The calculated *t*	**p-value** (2-tailed)
	Natural exposure condition	Accelerated condition			
Uncoated PS foam	57280	57617	12	0.019	0.985
1% Benzoyl peroxide coated PS foam	56659	55387	12	0.059	0.954

APPENDIX C

Statistical Table

Table C1 Critical value, $t_{1-\alpha,\ \nu}$ for the t distribution

ν	α						
	0.10	0.05	0.025	0.01	0.005	0.001	0.0005
1	3.078	6.314	12.706	31.821	63.657	318.31	636.62
2	1.886	2.920	4.303	6.965	9.925	22.326	31.598
3	1.638	2.353	3.182	4.541	5.481	10.213	12.924
4	1.533	2.132	2.776	3.747	4.604	7.173	8.610
5	1.476	2.015	2.571	3.365	4.032	5.893	6.869
6	1.440	1.943	2.447	3.143	3.707	5.208	5.959
7	1.415	1.895	2.365	2.998	3.499	4.785	5.408
8	1.397	1.860	2.306	2.896	3.355	4.501	5.041
9	1.383	1.833	2.262	2.821	3.250	4.297	4.781
10	1.372	1.812	2.228	2.764	3.169	4.144	4.587
11	1.363	1.796	2.201	2.718	3.106	4.025	4.437
12	1.356	1.782	2.179	2.681	3.055	3.930	4.318
13	1.350	1.771	2.160	2.650	3.012	3.852	4.221
14	1.345	1.761	2.145	2.624	2.977	3.787	4.140
15	1.341	1.753	2.131	2.602	2.947	3.733	4.073
16	1.337	1.746	2.120	2.583	2.921	3.686	4.015
17	1.333	1.740	2.110	2.567	2.898	3.646	3.965
18	1.330	1.734	2.101	2.552	2.878	3.610	3.922
19	1.328	1.729	2.093	2.539	2.861	3.579	3.883
20	1.325	1.725	2.086	2.528	2.845	3.552	3.850
21	1.323	1.721	2.080	2.518	2.831	3.527	3.819
22	1.321	1.717	2.074	2.508	2.819	3.505	3.792
23	1.319	1.714	2.069	2.500	2.807	3.485	3.767
24	1.318	1.711	2.064	2.492	2.797	3.467	3.745
25	1.316	1.708	2.060	2.485	2.787	3.450	3.725
26	1.315	1.706	2.056	2.479	2.779	3.435	3.707
27	1.314	1.703	2.052	2.473	2.771	3.421	3.690
28	1.313	1.701	2.048	2.467	2.763	3.408	3.674
29	1.311	1.699	2.045	2.462	2.756	3.396	3.659
30	1.310	1.697	2.042	2.457	2.750	3.385	3.646
40	1.303	1.684	2.021	2.423	2.704	3.307	3.551
60	1.296	1.671	2.000	2.390	2.660	3.232	3.460
120	1.289	1.658	1.980	2.658	2.617	3.160	3.373
∞	1.282	1.645	1.960	2.326	2.576	3.090	3.291

[Source: Devore, J.L. (1995)]

Table C2 Critical value $f_{\alpha, \nu 1, \nu 2}$ for the F distribution at $\alpha = 0.05$

ν2	ν1																		
	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45	19.45	19.46	19.47	19.48	19.49	19.50
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.77	5.75	5.72	5.69	5.66	5.63
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.15	2.07	1.99	1.95	1.90	1.85	1.80	1.75	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.13	2.06	1.97	1.93	1.88	1.84	1.79	1.73	1.67
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.12	2.04	1.96	1.91	1.87	1.82	1.77	1.71	1.65
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.10	2.03	1.94	1.90	1.85	1.81	1.75	1.70	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.50	1.43	1.35	1.25
∞	3.48	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

[Source: Devore, J.L. (1995)]