

**The Effect of Multiple-use of Polystyrene Cups on Styrene Monomer Migration**

by

Siti Nur Hidayah Binti Mat Salleh

Dissertation submitted in partial fulfilment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Mechanical Engineering)

JULY 2008

Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan

**CERTIFICATION OF APPROVAL**

**The Effect of Multiple-use of Polystyrene Cups on Styrene Monomer Migration**

by

Siti Nur Hidayah Binti Mat Salleh

A project dissertation submitted to the  
Mechanical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
(MECHANICAL ENGINEERING)

Approved by,

---

(Assoc. Prof. Dr. Puteri Sri Melor Bt Megat Yusoff)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2008

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

---

SITI NUR HIDAYAH BINTI MAT SALLEH

## **ABSTRACT**

Traces of styrene monomer are normally found in polystyrene (PS) cups due to incomplete reaction during their processing. This study was conducted to investigate the effect of multiple-use on styrene monomer migration from PS cup into the foodstuff it contained. Palm oil and distilled water were used as stimulants to promote the migration of styrene from the cups and to simulate the fatty and aqueous medium of beverages respectively. The cups were repetitively exposed to the stimulants at 100°C up to ten times. The stimulants were then tested for their styrene monomer content using gas chromatography-mass spectroscopy (GC-MS) technique. Analysis by GC-MS showed that styrene monomer was detected in the palm oil stimulant but undetected in the distilled water when the cups were subjected to repetitive use. The maximum concentration of styrene monomer measured in the palm oil was 161.74 ppb after the 6<sup>th</sup> repetition while the minimum level was 16.14 ppb measured after the 8<sup>th</sup> repetition. The maximum value of 161.74 ppb is exceeding the limit of WHO guideline value which might be harmful to the consumer under prolong and continuous exposure. The study has highlighted the negative effect of using PS cup repetitively especially in the presence of fatty medium. The effect may not be as bad if the cup contained only aqueous medium.

## ACKNOWLEDGEMENTS

First and foremost, I would like to praise God the Almighty for His guidance. Though difficulties occurred, His guidance gave me the chance to still complete my Final Year Project successfully. Here, I would like to use this special opportunity to express my heartfelt gratitude to everyone that has contributed and helped me throughout this phase.

My deepest appreciation particularly goes to my supervisor, **Assoc. Prof. Dr. Puteri Sri Melor Binti Megat Yusoff** who had advised and guided me throughout this project. I really acknowledged all the precious words from her. I would also like to address my thankfulness to many UTPs lecturers and staffs for their invaluable inputs which had helped me to conduct this research.

I also appreciate the assistance and cooperation given by groups of technician in Chemical Engineering and Mechanical Engineering Department who were involved either directly or indirectly in my project. Not to forget, my highest gratitude to my beloved family members and friends for feedback, support, as well as their useful advice. With their contribution, my project is completed comprehensively. Thank you.

## TABLE OF CONTENTS

<b>CERTIFICATION OF APPROVAL</b>	. . . . .	i
<b>CERTIFICATION OF ORIGINALITY</b>	. . . . .	ii
<b>ABSTRACT</b>	. . . . .	iii
<b>ACKNOWLEDGEMENTS</b>	. . . . .	iv
<b>CHAPTER 1:</b>	<b>INTRODUCTION</b>	1-2
	1.1 Background of Study	2
	1.2 Problem Statement	2
	1.2.1 Problem Identification.	2
	1.2.2 Significance of Study	3
	1.3 Objectives and Scope of Study	3
	1.3.1 Objective	3
	1.3.2 Scope of Study	3
<b>CHAPTER 2:</b>	<b>THEORY/LITERATURE REVIEW</b>	4
	2.1 Theory	4
	2.1.1 Polystyrene	4-5
	2.1.2 Styrene Monomer	5
	2.2 Literature review	6-8
<b>CHAPTER 3:</b>	<b>METHODOLOGY</b>	9
	3.1 Procedures Identification	9
	3.2 Materials	9
	3.3 Equipment and Tools	10
	3.4 Project Activities	10
	3.5 Material Characterizations	11
	3.5.1 Chemical Analysis	11
	3.5.2 Thermal Behaviour Analysis	11-12
	3.5.3 Sample Preparation and Multiple-use Investigation	13
	3.5.4 Styrene Monomer Migration Analysis	13
<b>CHAPTER 4:</b>	<b>RESULTS AND DISCUSSION</b>	
	4.1 Material Characterisation of the PS Cup	14
	4.1.1 Chemical Analysis	14-16
	4.1.2 Thermal Behaviour Analysis	16-17
	4.2 Physical Observation of the Used PS Cup	18-19
	4.3 Styrene Monomer Measurement	19
	4.3.1 Palm Oil Stimulant	19-22
	4.3.2 Distilled Water Stimulant	22-23

<b>CHAPTER 5:</b>	<b>CONCLUSIONS</b>	.	.	.	.	.	.	24
	5.1 Conclusions	.	.	.	.	.	.	24
	5.2 Recommendations	.	.	.	.	.	.	25
<b>REFERENCES</b>	.	.	.	.	.	.	.	26-28

**APPENDICES**

APPENDIX A: GANTT CHART

APPENDIX B: DATA FROM TGA ANALYSIS

APPENDIX C: FTIR DATA AND STANDARD ANALYSIS METHOD

APPENDIX D: DATA FROM GC-MS ANALYSIS

## LIST OF FIGURES

Figure 1-1: Polystyrene cup . . . . .	2
Figure 2-1: Polystyrene structure . . . . .	4
Figure 3-1: Palm oil and distilled water as food stimulants . . . . .	9
Figure 3-2: Methodology to investigate the effect of multiple-use of PS cup on styrene monomer migration . . . . .	10
Figure 3-3: Fourier transforms infrared spectroscopy . . . . .	11
Figure 3-4: Thermogravimetric analysis (TGA) machine . . . . .	12
Figure 3-5: Differential scanning calorimetry . . . . .	12
Figure 3-6: Gas chromatography and mass spectrometry . . . . .	13
Figure 4-1: Chemical structure of polystyrene plastic . . . . .	14
Figure 4-2: FTIR spectrum of polystyrene cup . . . . .	15
Figure 4-3: FTIR spectrum of styrene monomer . . . . .	15
Figure 4-4: Weight loss of PS cup versus temperature profile for PS cup . . . . .	16
Figure 4-5: DSC curve of polystyrene cup . . . . .	17
Figure 4-6: PS cup sample for palm oil stimulant after eight repetitions . . . . .	18
Figure 4-7: PS cup sample for distilled water stimulant after the ten repetitions . . . . .	18
Figure 4-8: Chromatograms spectra of palm oil showing the effect of multiple-use . . . . .	20
Figure 4-9: A plot of styrene monomer concentration versus number of repetitions . . . . .	21
Figure 4-10: Typical spectrum for distilled water stimulant . . . . .	23



## LIST OF TABLES

Table 2-1: Application of polystyrene plastic	. . . . .	4
Table 2-2: Properties of styrene	. . . . .	5
Table 4-1: Chemical assignment for PS cup obtained from FTIR spectroscopy	. . . . .	16
Table 4-2: Weight of PS cups sample at the beginning and at the end of the experiment	. . . . .	19
Table 4-3: Styrene monomer concentration in palm oil stimulant	. . . . .	21

## LIST OF ABBREVIATIONS

<b>Abbreviations</b>	<b>Full Name</b>
PS	Polystyrene
WHO	World Health Organization
EPA	Environmental Protection Agency (US)
FDA	Food and Drug Administration (US)
MCLG	Maximum Contaminant Level Goals
GPPS	General Purpose Polystyrene
HIPS	High Impact Polystyrene
GC-MS	Gas Chromatography- Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
KBr	Potassium Bromide
ppm	part per million
SIM	Selected Ion Monitoring
SML	Specific Migration Limit

## NOMENCLATURES

<b>Symbol</b>	<b>Nomenclature</b>	<b>Units</b>
T	Temperature	°C
T <sub>o</sub>	Onset temperature	°C
T <sub>g</sub>	Glass transition temperature	°C
T <sub>m</sub>	Melting temperature	°C
$\lambda$	Wavelength	cm <sup>-1</sup>

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Polystyrene (PS) plastics have been widely used for many years as food packaging materials. There are two forms of polystyrene available in the industry, specifically foam and solid. Foamed polystyrene is used for manufacturing cups, bowls, plates, trays and egg cartons while the solid form is found in products such as cutlery, yogurt containers and compact disc cases. The application of polystyrene container varies in range of temperature, from low temperature for longer period, for example packaged dairy and meat products, to high temperature approaching the boiling point of water for short period of time, for example vending cups.

However, the usage of these plastic packaging as food and beverages containers must comply with the safety requirements of European Directives to prevent any side effects on the food that have direct contact with the plastic surface [1]. From previous research, there was evidence that substances used to make plastics can leach into food from direct contact with plastic surface. In a study by Abd Rahim Mohamad from Department of Public Health, Health Ministry on food containers made from plastics and polystyrene have found that 45 out of 47 plastic containers have at least one chemical detected in their leachate including styrene [2].

The principal classes of substances, which can migrate from polystyrene plastics to foods and beverages, are residual styrene monomers, low molecular weight components which are called oligomers and various additives. Substances migrating to foodstuffs are of concern if they present a possible health hazard to the consumer, or cause unacceptable changes to the properties of the food or beverage [3]. Therefore

experimental approaches were developed to investigate and identify the presence of styrene in the food samples. Figure 1-1 illustrates the polystyrene cup which is used in the study to investigate the migration behaviour of styrene monomer in the cup.



Figure1-1: Polystyrene cup.

## **1.2 Problem Statement**

### **1.2.1 Problem Identification**

Polystyrene cups are widely used as packaging material especially in the food industry due to its convenience and low cost. However, there is a concern in their usage particularly under multiple or repeated use. It is because, by using the PS cup repetitively may degrade the cup and cause chemical components such as styrene monomer to be released from the container. Most people use polystyrene container repetitively for convenience and cost saving without considering the danger of chemical substance migrating into the food after prolonged and repetitive use.

Styrene is potentially carcinogenic and can adversely affect human health. This raises serious public concerns on its build-up in human tissue and the root cause of this build-up needs to be ascertained. Long term exposure to small quantities of styrene can cause neurotoxin such as fatigue, nervousness and sleeplessness. Low level exposure can occur through the ingestion of food products packaged in PS containers.

In 2006, the ex-Health Minister of Malaysia, Dr. Chua Soi Lek once had advised consumer to stop reusing plastic food and water containers. He said this was because the quality of such products was “questionable” and Malaysians were at risk of being

exposed to chemicals which might leach into the food or liquid [4]. Considering the importance of toxic effect of styrene monomer and its migration into beverages from PS cup, the present study was conducted.

### **1.2.2 Significance of Study**

In this study, migration of styrene monomer from polystyrene cup as the consequence of repeated use of the cup will be investigated. This research is substantial as the findings can be of practical interest to consumers and food packaging industry. The outcome of this study will give better perspective on the use of polystyrene cup. More importantly, the result of the study may reduce user's risks from developing harmful and lethal diseases such as cancer.

## **1.3 Objectives and Scope of Study**

### **1.3.1 Objective**

Styrene monomer residues are normally found in PS cups due to incomplete reaction during their manufacturing process. This project was conducted to investigate the effect of multiple-use of PS cup on styrene monomer migration from the cup to its content.

### **1.3.2 Scope of Study**

In the study, PS cup bought from the local market and manufactured by Zhaori were used. Two types of stimulant were employed, specifically the distilled water and the palm oil to promote the migration process and to simulate the fatty and aqueous medium of beverages. It is because the food medium and type of contact between the packaging surfaces will influence the extent of concentration of any chemical migration that might occurs. In order to simulate the multiple-use effect, the cups were exposed repetitively to each stimulant at 100°C up to ten times. The cups containing stimulant were left at ambient temperature for one hour. The purpose was to maintain the same atmospheric conditions in which these cups are used in daily life. The used stimulant was then measured for its styrene monomer content.

## CHAPTER 2

### THEORY/LITERATURE REVIEW

#### 2.1 Theory

##### 2.1.1 Polystyrene

Polystyrene is a plastic created from ethyl benzene that can be injected, extruded or blow molded, making it a very useful and versatile manufacturing material. It is the parent polymer of a family of styrene-based plastics which are used for the manufacture of items ranging from furniture and electrical goods, toys, house wares and a wide variety of packaging material for foods and beverages industry. Table 2-1 summarizes the application of polystyrene plastic.

Table 2-1: Application of polystyrene plastic.

Food Related Applications of PS	Non-Food Related Applications of PS
<ul style="list-style-type: none"> <li>• coffee cups</li> <li>• soup bowls and salad boxes</li> <li>• foam egg cartons and meat trays</li> <li>• disposable utensils</li> </ul>	<ul style="list-style-type: none"> <li>• foam inserts to cushion new appliances and electronics</li> <li>• television and computer cabinets</li> <li>• compact disc and audiocassette cases</li> </ul>

Polystyrene is a vinyl polymer consists of long hydrocarbon chains, with a phenyl group attached to every other carbon atom. Polystyrene is produced by free radical vinyl polymerization, from the monomer styrene as shown in Figure 1 [5].

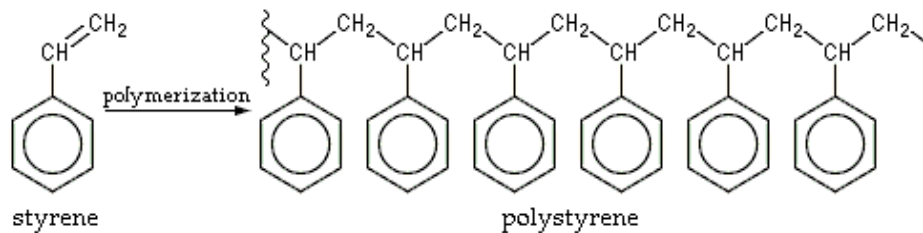


Figure 2-1: Polystyrene structure.

A major use of polystyrene plastics is in expanded sheet form. Expanded polystyrene plastics are extensively employed as general protective packaging, sometimes called cushioning packaging, but they also find wide use as packaging for food formed into trays and containers such as disposable beverage cups [6]. The expanded polystyrene plastics used for these applications are known as foamed polystyrenes.

### 2.1.2 Styrene Monomer

Styrene monomers are the starting chemical substances from which polystyrene polymer are produced. Additives are incorporated to convert polystyrene polymer into plastics with the required physical properties to be used as packaging for foodstuffs. Styrene is an organic compound most commonly produced by the catalytic dehydrogenation of ethylbenzene [7]. Under normal conditions, this aromatic hydrocarbon is an oily liquid. It evaporates easily and has a sweet smell, although common impurities give pungent and unpleasant odor [8]. Table 2-2 summarizes the properties of styrene monomer.

Table 2-2: Properties of styrene [9].

Property	Description
Chemical Structure	$C_8H_8$
Molecular weight	104.4
Boiling point	145.2°C
Freezing point	- 30.63°C
Solubility	0.31g in 100 ml of water, miscible with most organic solvents
Standards and Legislation	World Health Organization (WHO) limit is 20 µg/l, Food and Drug Administration (FDA) sets no specific migration limit (SML), thus controlled by overall migration limit of 60 mg/kg  <u>WHO claims:</u> "Acute exposure to styrene in humans results in mucous membrane and eye irritation, and gastrointestinal effects. Chronic exposure to styrene in human results in effects on the central nervous system (CNS), such as headache, fatigue, weakness, and depression, CSN dysfunction, hearing loss, and peripheral neuropathy".
Hazard risk	Classified according to DIN4102 as a "B3" product, meaning highly flammable or easily ignited.



## 2.2 Literature Review

Materials such as plastics are commonly used for the manufacturing of consumer goods and food packaging. The safety of such materials relates to the amount of chemical substances migrating into the food during contact with the plastic surface. Food packaging is intended for single use only. In reality however, packaging may be reused to contain food other than those initially intended and in some cases, used under direct heating.

Apparently, the polystyrene cup can lose weight after a single usage due to styrene migration into the foodstuff. Therefore, common practice of using and re-using disposable polystyrene cup for a long period is not advisable. Scientific studies have found that repeated use of such plastic container is subjected to surface damage through normal wear and tear while being washed. This is because repeated washing and rinsing can cause the plastic to break down and it will increase the chance of chemicals leaking out of the tiny cracks and crevices that developed over time [10]. As a result, potential carcinogens such as styrene can leach into the drinking water or food.

Styrene monomer is primarily used in the production of polystyrene plastics and resins. Styrene monomer which is a hazardous compound that leaches out from polystyrene cups and containers into fatty food or drink can cause a potential health risk to people. Styrene leaching out from polystyrene containers into the food can be detrimental to human health and reproductive systems. Short term or acute exposure to styrene in humans results in mucous membrane and eye irritation, and gastrointestinal effects. While long term or chronic exposure to styrene in human create symptoms such as headache, fatigue, weakness and depression [11].

Styrene primarily exhibits its toxicity to humans as a neurotoxin by attacking the central and peripheral nervous systems. The accumulation of these highly lipid-soluble materials in the lipid-rich tissues of the brain, spinal cord, and peripheral nerves is correlated with acute or chronic functional impairment of the nervous system. EPA National Human Adipose Tissue Survey for 1986 identified styrene residues in 100% of

all samples of human fat tissue taken in US. Research also indicates that toxic chemicals in polystyrene products can have long-term consequences on the reproductive systems of both men and women. Women exposed to low concentrations of styrene are known to demonstrate menstrual disorders, particularly perturbations of the menstrual cycle and a hypermenorrhea syndrome which is unusually heavy flow of menses during the menstrual cycle [12].

Numerous studies and investigations have been carried out to determine levels of migration of styrene monomer into foods and beverages from the various polystyrene plastics used for food packaging and for beverage containers. Comprehensive survey on styrene levels in food contact materials and migrations into foods in the Eleventh Report of the Steering Group on Food Surveillance had highlighted the fact that although residue levels of styrene monomer in the various polystyrene plastics were found to be as high as 0.1% by weight (1,000 mg/kg), the quantities determined in the foods and beverages which came into contact with the plastics due to migration were relatively low. The mean styrene values found in various food types were in the region of 10 ppb ( $\mu\text{g}/\text{kg}$ ), with maximum levels around 200 ppb ( $\mu\text{g}/\text{kg}$ ) [13].

Another study by UK MAFF in 1992 and 1994 on styrene levels in packaging and migrations into packaged foods revealed that the levels of styrene monomer in foodstuffs which had come into contact with polystyrene plastics ranged from not detectable to 60 ppb ( $\mu\text{g}/\text{kg}$ ) where 248 samples of foods were examined during the study [14]. The study concluded that the levels of styrene present in the foodstuffs could not be related to any one particular factor. It was stated that the levels varied, for instance, with the nature of the food, the level of residual styrene in the container and the length and temperature of storage.

In 1996, WHO has set the limit on styrene concentration in drinking water as 0.02 mg/l. However, the FDA has determined that the styrene concentration in bottled drinking water should not exceed 0.1 ppm. While in 1999, the U.S. EPA determined that lifetime exposure to 0.1 ppm styrene was not expected to cause any adverse effects to human.

These non-enforceable levels, based solely on possible health risks and exposure, are called Maximum Contaminant Level Goals. The MCLG for styrene has been set at 0.1 parts per million (ppm) because EPA believed that this level of styrene exposure would not cause any of the potential health problems as have been described above [15].

In a study by Tawfik MS [16], the level of styrene migration from polystyrene cups was monitored in different food systems including water, milk, cold and hot beverages, soup, take away foods and olive oil. The results concluded a maximum observed migration of 0.025% of the total styrene in the cup [16]. The value may seem low, however the damage is accumulative and it increases as use of polystyrene cups increases. This is because styrene is distributed through the whole human body and stored in lipid depots and its subsequent slow elimination from the tissue indicates a potential for bioaccumulation following repeated daily exposure [17].

Another research by M. Ghazi-Khansari and M.Khaksar [18] has shown that migration of styrene monomer was higher with fatty foods than with aqueous foods. Styrene migration has been shown to be partially dependent on the fat content of the food in the polystyrene container. The hypothesis was the higher the fat content, the higher the migration into the food. The amount of migration of styrene monomer from general purpose polystyrene (GPPS) and high impact polystyrene (HIPS) cups to milk with fat content 3.6% was greater than fat content of 1.5% and 2.5 %. In this study, the average range of styrene migration into milk at different temperature and time were between 0.2-8.42  $\mu\text{g/l}$ . Also the greatest amount of migration of styrene monomer was observed in the first 10 minutes of experiments [18].

## CHAPTER 3

### METHODOLOGY/PROJECT WORK

#### 3.1 Procedures Identification

Initially, material characterization was done on the PS cup by performing chemical analysis and thermal behaviour analysis. Next, multiple-use investigation was conducted in which PS cups were exposed to stimulants at 100°C and left at ambient temperature for one hour. The experiment was repeated up to 10 times with two different stimulants specifically distilled water and palm oil. Then, the used stimulants were analyzed to detect the existence of styrene migration by using GC-MS.

#### 3.2 Materials

PS cups sample used in this experiment were manufactured by Zhaori and were purchased from the local market. Meanwhile, Vesawit brand palm oil and distilled water as shown in Figure 3-1 were used as stimulants to promote the styrene migration in the study.



Figure 3-1: Palm oil and distilled water as food stimulants.

### 3.3 Equipment and Tools

Equipments and tools used throughout this research were fourier transform infrared spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential scanning calorimetry (DSC) and gas chromatography and mass spectrometry (GC-MS). FTIR was used to identify the chemical composition of PS cup. Thermal properties characterization of the PS cup was done using TGA and DSC while, GC-MS was used for chemical analysis of the used stimulant to detect styrene migration.

### 3.4 Project Activities

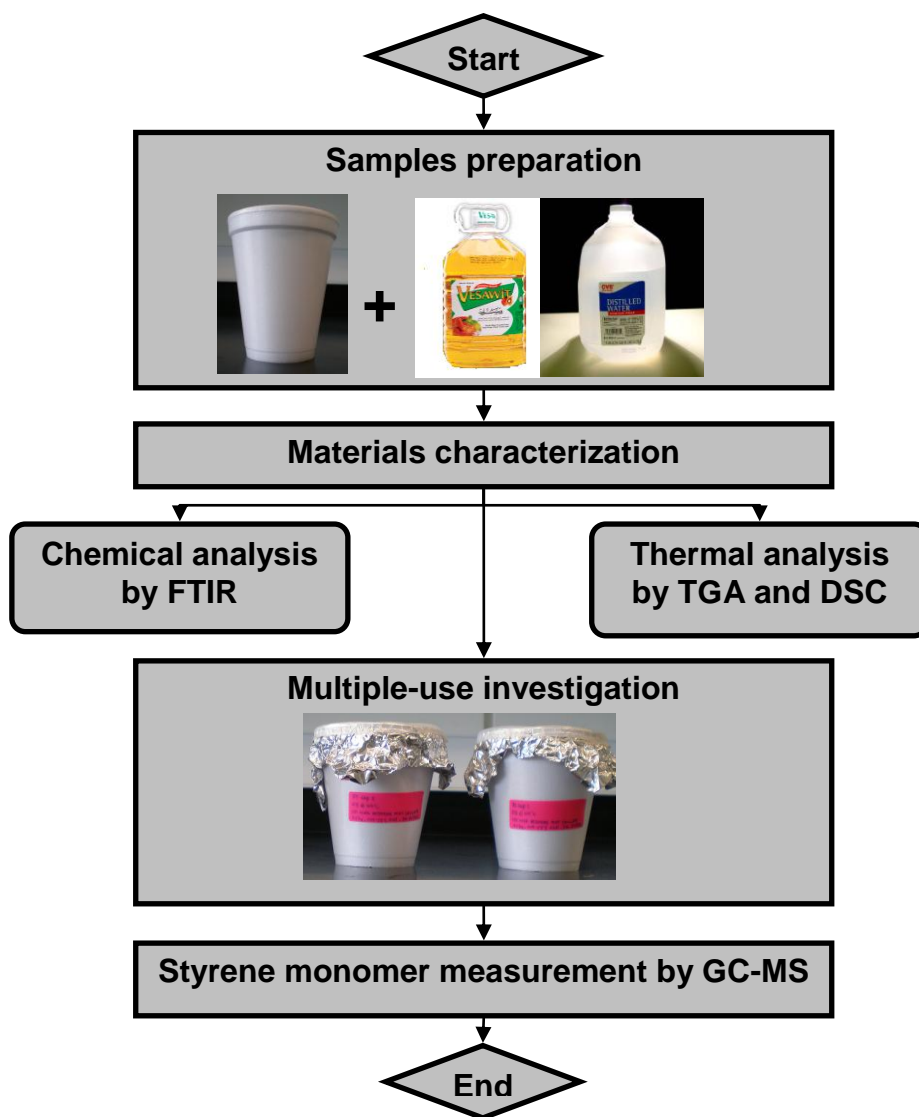


Figure 3-2: Methodology to investigate the effect of multiple-use of PS cup on styrene monomer migration.

### 3.5 Material Characterizations

#### 3.5.1 Chemical Analysis

The chemical composition of control sample of polystyrene cup was analyzed using FTIR spectroscopy. Sample (PS cup) was milled with potassium bromide (KBr) to form a very fine powder, and then compressed into a thin clear pallet. In order to identify the chemical composition of the polystyrene cup, the thin pallet was placed into the FTIR machine and the infrared intensity versus wavelength ( $\lambda$ ) was measured. Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a specific wavenumber range of the sample. The correlation of the band wavenumber position with the chemical structure is used to identify a functional group in the sample. Liquid samples were analyzed using a FTIR Perkin–Elmer spectrometer while solid sample is analyzed using a FTIR Shimadzu. The spectra were recorded in the spectral range of 600–3500  $\text{cm}^{-1}$ .



Figure 3-3: Fourier transforms infrared spectroscopy.

#### 3.5.2 Thermal Behaviour Analysis

##### 3.5.2.1 Thermogravimetric Analysis (TGA)

TGA method was used to study the thermal decomposition behaviour of the PS cup. In this case, TGA analysis was performed in an oxidative atmosphere of oxygen and inert gas mixtures with a linear temperature ramp. The maximum temperature of 900°C was selected so that the specimen weight was stable at the end of the experiment, implying that all chemical reactions were completed. The technique provides information on the

degradation and decomposition of the PS cup in the form of weight loss against temperature.



Figure 3-4: Thermogravimetric analysis (TGA) machine.

#### ***3.5.2.2 Differential Scanning Calorimetry (DSC).***

Differential scanning calorimetry was used to characterize the thermal properties such as glass transition temperatures ( $T_g$ ) and melting temperature ( $T_m$ ) of the polystyrene cup. Sample was cut into extremely small pieces, and then it was enclosed in a special aluminium pans with mass ranging from 5 to 10 mg. Next, the aluminium pan was placed into the DSC while the initial temperature is set at  $25^{\circ}\text{C}$  and the final temperature is set at  $260^{\circ}\text{C}$  with heating rate of  $20^{\circ}\text{C}$ .



Figure 3-5: Differential scanning calorimetry.

### 3.5.3 Sample Preparation and Multiple-use Investigation

In this experiment, PS cups were filled with either 100 ml of distilled water or palm oil at 100°C; 1 cup was employed for each stimulants. The cups were covered with aluminum foil and their lid. Each of the cups were labeled and left at ambient temperature for one hour. Then, the used stimulants were gathered for styrene monomer measurement. The cups were washed after each run as to prepare for subsequent experiments to simulate the multiple-use. The experiment was repeated up to ten times.

### 3.5.4 Styrene Monomer Migration Analysis

A headspace gas chromatographic method was used to analyze the migration of styrene monomer from polystyrene container into foodstuffs. Both of the samples; distilled water and cooking oil were examined using GC-MS. Analysis was performed by gas chromatography (GC) with mass spectrometry detection, using a Shimadzu GC14A, a SPB-5 capillary column (30mlong×0.32mmi.d.), a split–splitless injector and a quadrupole mass spectrometer. Helium was used as the carrier gas, with a head pressure of 153 KPa. Temperatures for injector and detector were 300°C and 250°C respectively, and the column temperature was programmed from 35°C (hold 10 min) to 150°C at a 7°C/min heating rate to 220°C (hold 6 min) at a 20°C/min heating rate. Samples were injected in the splitless mode and after closure, the vial was shaken for 30 minutes at 60°C. Quantification of styrene was performed in selected ion monitoring (SIM) mode focused on 104 (main) and 78 ions, by comparing chromatographic peak areas for the sample with the calibration curve the styrene monomer standard.



Figure 3-6: Gas chromatography and mass spectrometry.



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Material Characterization of the PS cup

##### 4.1.1 Chemical Analysis

A sample of the PS cup and a styrene monomer standard were analysed by FTIR spectroscopy. Comparison of both spectra of the PS cup and the styrene monomer standard allows evaluation of the vibration mode of chemical bonding such as phenyl ring groups,  $-C=C-$ ,  $C-H_2$  and  $C-H$  stretching which constitute the polystyrene structure as shown in the Figure 4-1.

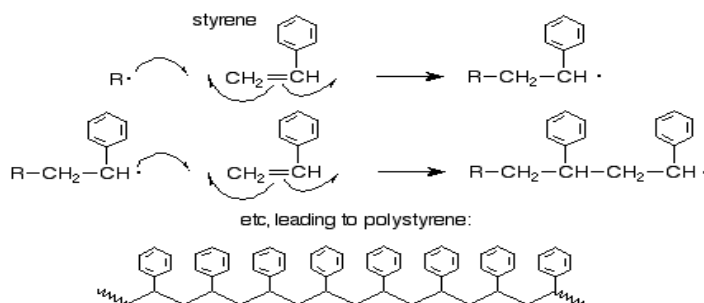


Figure 4-1: Chemical structure of polystyrene plastic.

To monitor the presence of styrene in the spectrum, focus is set on  $C=C$  (double bonds) from an aromatic ring and phenyl ring substitution. Aromatic ring  $C=C$  stretching appears as medium absorptions in the region of  $1604-1495\text{ cm}^{-1}$  in spectrum of PS cup sample while for standard styrene monomer, it can be observed in the region of  $1629-1493\text{ cm}^{-1}$ . Phenyl ring groups occurred in the region of  $727-692\text{ cm}^{-1}$  in the PS cup sample, while for standard styrene monomer at  $774-690\text{ cm}^{-1}$  with strong and sharp absorption.

Referring to Figure 4-2 and Figure 4-3, C=C in plane vibration for both spectra appear at  $1456\text{cm}^{-1}$  and  $1449\text{cm}^{-1}$  respectively. Stretching vibrations of C-H occurred at  $3086\text{--}2872\text{cm}^{-1}$  as fingerprint region in PS cup spectrum. Similarly, for standard styrene monomer, the fingerprint region is  $3081\text{--}2980\text{cm}^{-1}$ . Bending vibration of C-H<sub>2</sub> occurred at  $1378\text{cm}^{-1}$  with sharp peak. While for standard styrene monomer is at  $1412\text{cm}^{-1}$  also with sharp peak. Table 4-1 summarizes the chemical assignment resulted from the spectra.

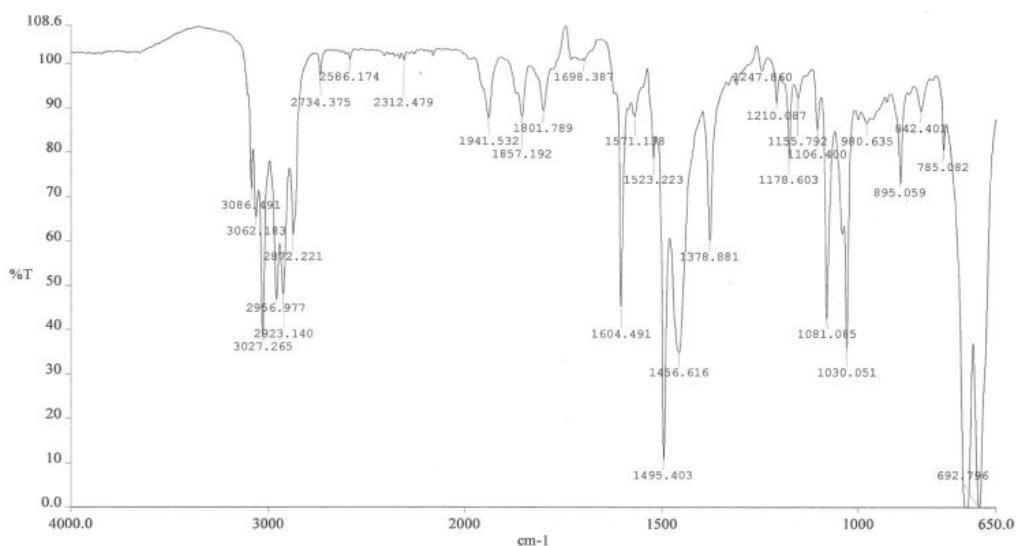


Figure 4-2: FTIR spectrum of polystyrene cup.

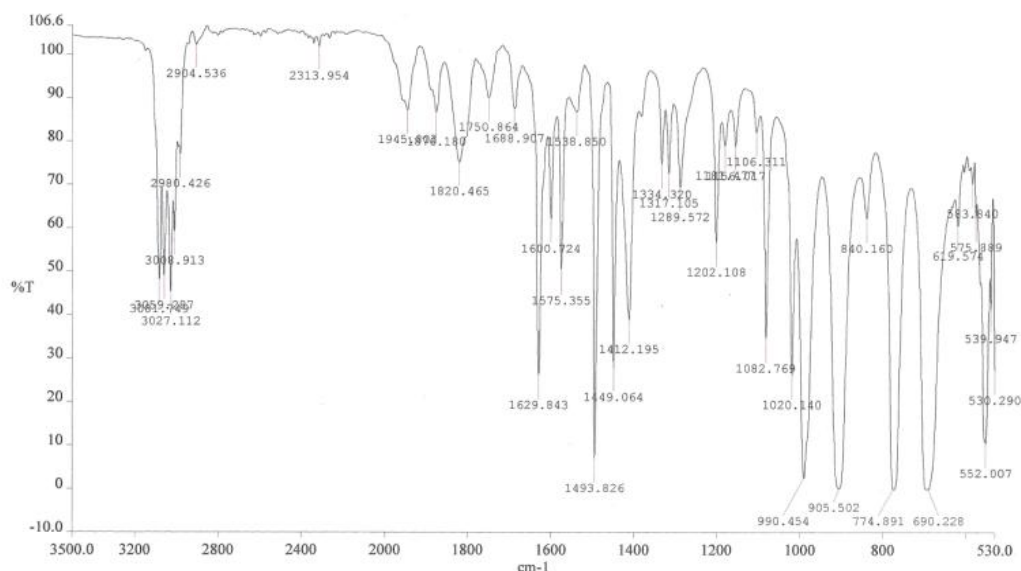


Figure 4-3: FTIR spectrum of styrene monomer.

Table 4-1: Chemical assignment for PS cup obtained from FTIR spectroscopy.

Peak assignment	Wavenumber/cm <sup>-1</sup> PS cup	Wavenumber/cm <sup>-1</sup> Styrene Monomer
Phenyl ring	727-692 (s) (sh)	774-690 (s) (sh)
-C=C- in plane vibration	1456 (w)	1449 (w)
Aromatic C=C stretch	1604-1495 (m)	1629 -1493 (sh)
C-H stretching vibration	3086-2872 (w)	3081-2980 (w)
C-H phenyl ring substitution vibration	1941-1698 (w)	1945-1688 (w)
C-H <sub>2</sub> bending vibration	1378 (sh)	1412 (sh)

(w)- weak peak, (m)- medium strong, (s)- strong peak, (b)-broad, (sh)- sharp peak

#### 4.1.2 Thermal Behaviour Analysis

The thermal behaviour of the PS cup was studied by means of thermogravimetric (TGA) and differential scanning calorimetry (DSC). Thermogravimetric curves of the PS cup are given in Figure 4-4. Thermal decomposition of each sample took place in a programmed temperature range of 25–900°C. Decomposition of polystyrene cup started at 280°C and was completed at a temperature of 450°C. Figure 4-4 indicates that the major degradation occurs at temperature of 398°C.

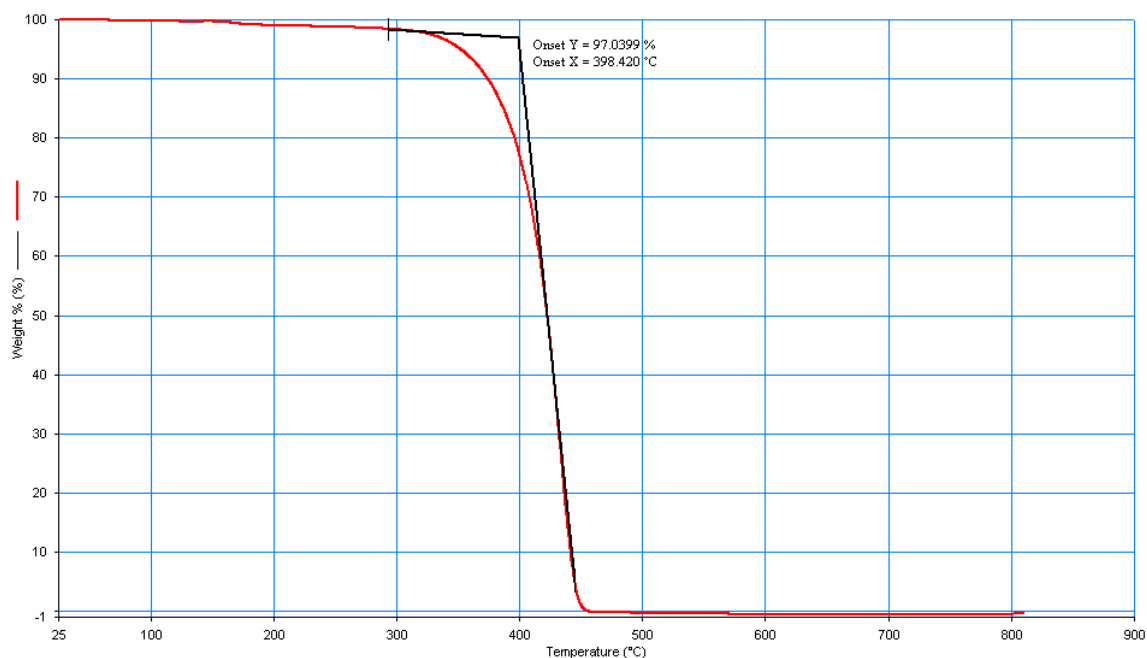


Figure 4-4: Weight loss of PS cup versus temperature profile for PS cup.

DSC curve of the PS cup is shown in Figure 4-5. The curve is of heat flux versus temperature. Referring to Figure 4-5, the glass transition temperatures ( $T_g$ ) for PS cup was observed at 102°C which is within the range of theoretical value of  $T_g$  for polystyrene polymer. As the temperature increases the sample eventually reaches its melting temperature. However there is no melting temperature detected which is expected to be observed at 270°C.

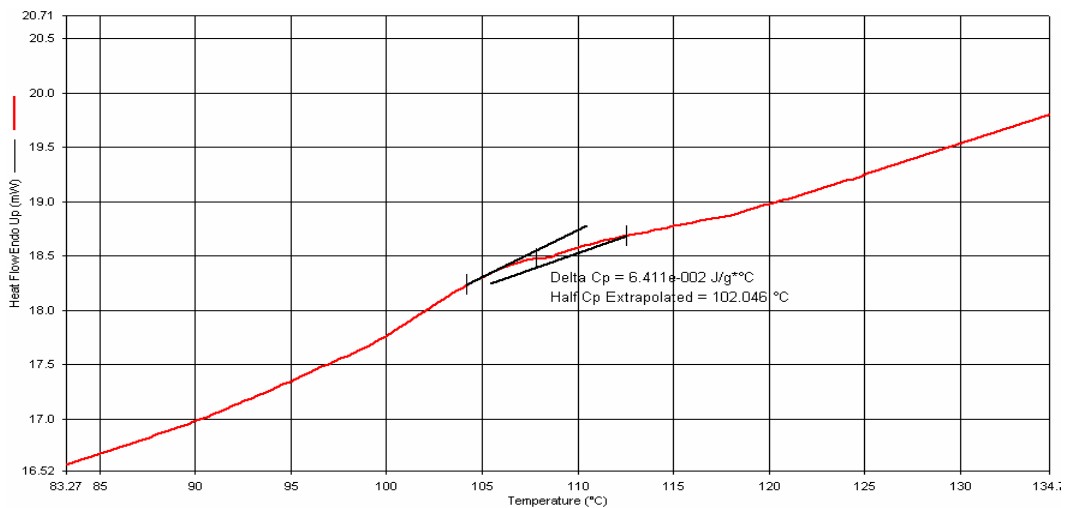


Figure 4-5: DSC curve of polystyrene cup.

In the thermal behaviour analysis, the glass transition temperature ( $T_g$ ) for PS cup was slightly higher even though the peak was very small. This is because the glass transition temperature depends on the cooling-ratio, molecular weight distribution and could be influenced by additives present in the cup. However, the value for  $T_g$  is still within the range of theoretical value therefore it was acceptable.

#### 4.2 Physical Observation of the Used PS Cup

In this experiment the physical appearance of the PS cups were observed after each experiments for both stimulants. Initially, the inside surface of the PS cups were smooth but during the sixth repetition they began to be coarse and patchy. This condition was observed for both stimulants.

The PS cup used for palm oil stimulant was structurally damaged at the end of the eighth repetition. However, PS cup sample used to contain the distilled water stimulant was in good shape throughout the experiment which was repeated up to ten times. Figure 4-6 shows the cup sample used to contain the palm oil stimulant and Figure 4-7 shows the cup sample used to contain the distilled water stimulant.



Figure 4-6: PS cup sample used to contain the palm oil after eighth repetition.

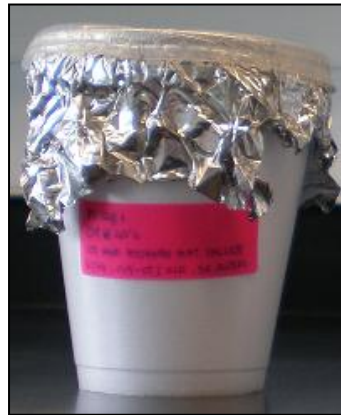


Figure 4-7: PS cup sample used to contain the distilled water after tenth repetition.

Both of the cups were also weighted at the beginning and at the end of the experiment. Apparently the weight of the cups was observed to reduce significantly after the experiment as summarised in Table 4-2. PS cup used with palm oil stimulant showed 7.3% reduction from initial weight while for PS cup used with distilled water stimulant the reduction was 4.6% of initial weight.

Table 4-2: Weight of PS cups sample at the beginning and at the end of the experiment.

<b>PS Cup</b>	<b>Weight Before</b>	<b>Weight After</b>	<b>Difference</b>	<b>Percentage</b>
Used with palm oil	2.59 g	2.40 g	0.19 g	7.3%
Used with distilled water	2.59 g	2.47 g	0.12 g	4.6%

From physical observation of the PS cups, the damaged cup could lead to higher styrene migration due to open and damaged structure of the cup. In order to verify this, further analysis using GC-MS was conducted to determine the amount of styrene migration.

### **4.3 Styrene Monomer Measurement**

Analysis on styrene monomer content in both stimulants was conducted using GC-MS where quantification of styrene monomer was performed in selected ion monitoring (SIM) mode focused on 104 (main) and 78 ions. By comparing the chromatographic peak areas with the calibration curve of the internal standard for styrene monomer, the concentration of styrene monomer present in each stimulant can be calculated.

#### **4.3.1 Palm Oil Stimulant**

The main work was to assess the extent to which styrene has leached from the PS cup into the foodstuff it contained when subjected to repetitive use. Results show that the migration of styrene monomer was significantly higher in fatty foods. Figure 4-8 shows the GC-MS spectra for palm oil stimulant after each repetition. Meanwhile, Table 4-3 summarizes the concentration of styrene monomer traced in the palm oil stimulant after each repetition.

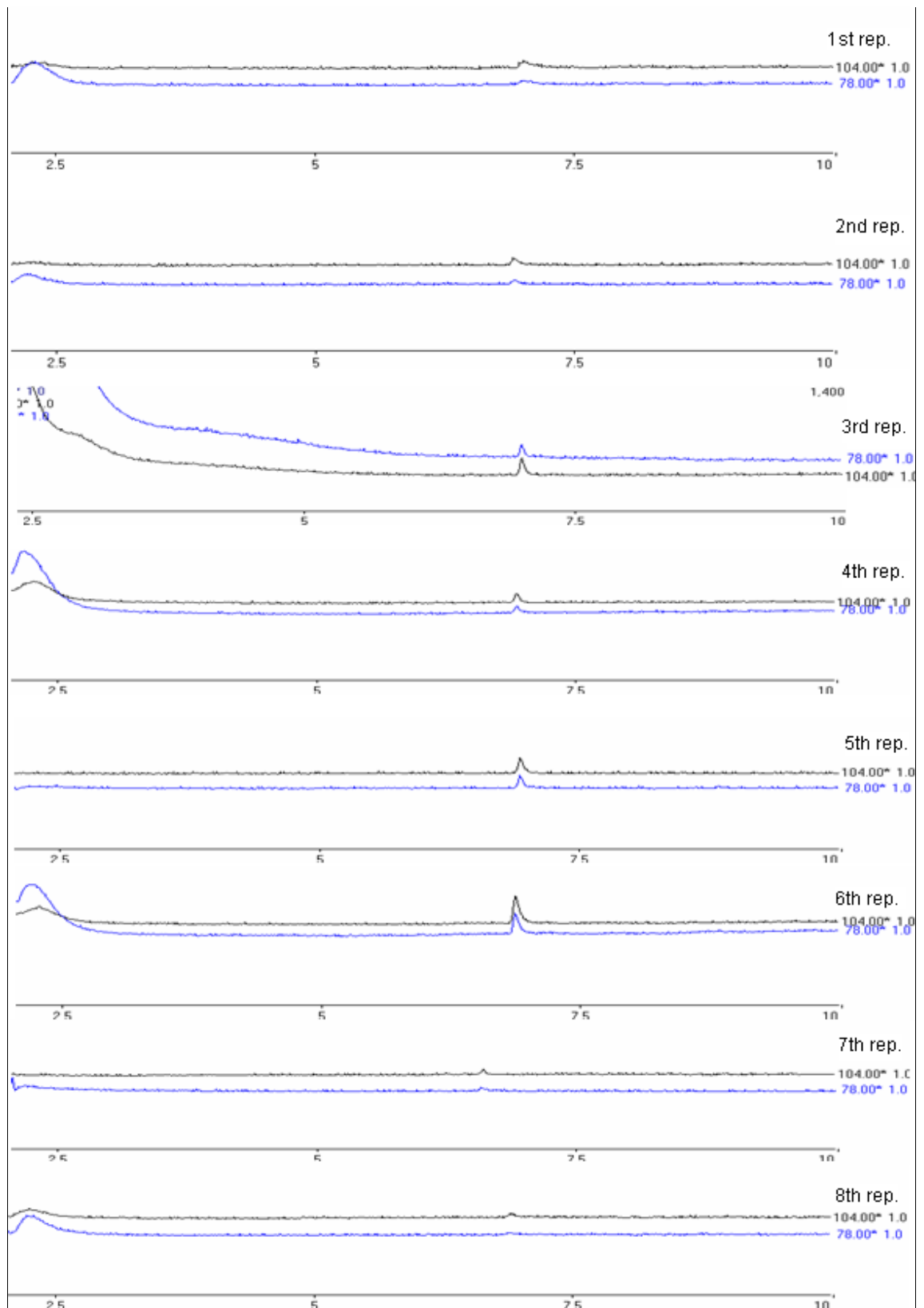


Figure 4-8: Chromatograms spectra of palm oil showing the effect of multiple-use.

Table 4-3: Styrene monomer concentration in the palm oil stimulant.

Repetition	Concentration (ppb)
1	45.3
2	36.06
3	21.6
4	58.1
5	82.09
6	161.74
7	19.85
8	16.14

In order to analyse the results further, the styrene monomer concentration measured after each repetition is plotted, as shown in Figure 4.9.

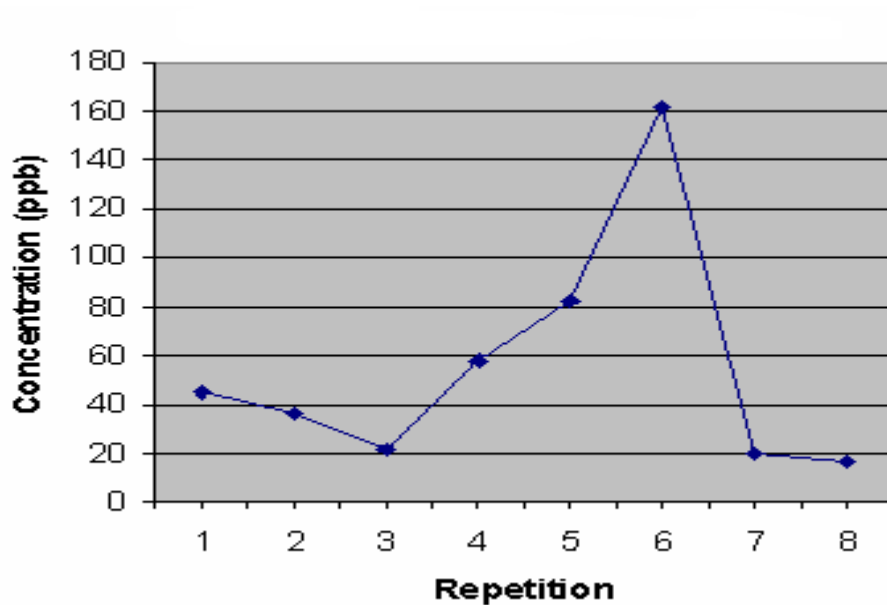


Figure 4-9: A plot of styrene monomer concentration versus number of repetitions.

From Figure 4-9, it can be observed that the amount of styrene monomer detected in the palm oil varied with number of repetition of the test. Initially, the concentration of styrene monomer decreased as the test was repeated up to three times but exhibit a remarkable increase at the 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> repetition. The initial decrease may be contributed from the slow release of the residual styrene monomer resulted from incomplete polymerisation process during manufacturing of the cup.



However, beginning at 4<sup>th</sup> repetition, the plastic cup may have experienced degradation and resulted in higher residual styrene monomer migrating out from the cup. Physical damage of the cup also contributed to the high amount of styrene monomer measured on the 6<sup>th</sup> repetition. After the observation of maximum value of 161.74 ppb, subsequently minimum level of styrene monomer was measured at 7<sup>th</sup> and 8<sup>th</sup> repetition possibly because there was not much monomer left in the cup to leach out. Overall, the total styrene monomer migrated from the 1<sup>st</sup> to 8<sup>th</sup> repetitions were 440.88 ppb.

Current European legislation sets no specific migration limit (SML) for styrene in food which means its content is then controlled by the overall migration limit of 60 mg/kg in the food [19]. However, the maximum value of 161.74 ppb is found to be exceeding the limit of WHO guideline maximum permissible limit of 20 ppb ( $\mu\text{g/l}$ ). The level is unsafe for consumer consumption. It may not have immediate effect but chronic effects may be observed as a result of repeated ingestion of a number of small doses, each in itself insufficient to cause an immediate acute reaction but in the long term having a cumulative toxic effect. As reported in literature, styrene is distributed throughout the body, with the highest concentration generally found in adipose tissue [17].

#### 4.3.2 Distilled Water Stimulant

Figure 4-10 shows the typical spectrum from GC-MS analysis for distilled water stimulant obtained from the study.

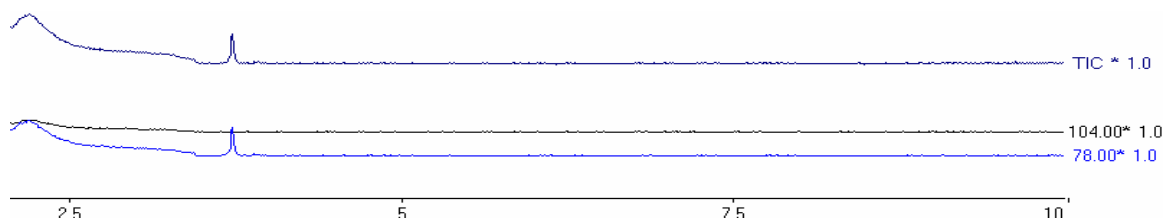


Figure 4-10: Typical spectrum for distilled water stimulant.

In distilled water, the migration of styrene monomer might be very small to be detected by the GC-MS. This is due to physical properties of the styrene monomer which has low solubility in water and can easily escape from the surface of hot water due to high vapour pressure and through volatilization [20].

The findings showed that no styrene monomer detected in the distilled water even though the test has been repeated up to ten times. It may indicate that no styrene monomer migrated from the cup if it contained only aqueous medium or the amount of styrene monomer was too small to be detected by the GC-MS as being described above. Therefore, further study is needed to verify if there is migration of styrene monomer in distilled water.

## **CHAPTER 5**

### **CONCLUSIONS**

#### **5.1 Conclusions**

The multiple use of polystyrene cup is questionable as there is a risk of residual styrene monomer migrating into the beverage it contained. Styrene monomer may be carcinogenic and can cause health problem to consumers. This research was conducted to investigate the effect of multiple-use of PS cup on styrene monomer migration from the cup to its content. Palm oil and distilled water were used as the stimulants to simulate the fatty and aqueous medium of beverages. In the investigation, 100 ml of stimulant was heated to 100°C before being placed in the PS cup and left at ambient temperature for one hour. The experiment was repeated up to ten times for each stimulant using the same cup. The used stimulants after each repetition were gathered and further analysed with GC-MS to measure the amount of styrene monomer migrated into each stimulant. Styrene monomer was indeed detected and measured in the palm oil but not in the distilled water. The maximum concentration of styrene monomer measured in the palm oil was 161.74 ppb at 6<sup>th</sup> repetition while the minimum level measured was 16.14 ppb at 8<sup>th</sup> repetition. The maximum value of 161.74 ppb is exceeding the limit of WHO guideline maximum permissible limit of 20 ppb ( $\mu\text{g/l}$ ), which might be harmful to the consumer under prolong and continuous exposure. The maximum amount of styrene monomer measured correlated to the physical damage experienced by the cup due to wear and degradation effect of the repetitive use. Therefore, it is concluded that PS cup should not be used repetitively as styrene monomer may migrate into its content especially for food or beverage with high fat content.

## **5.2 Recommendations**

For further research work, it is recommended to vary the food representation such as to use milk, yogurt or other relevant foodstuff to give variability and to replicate the real life situation. It is because the level of styrene migration was found to be varied according to the nature of the food. Another important factor that needs to be considered is to add more parameters such as temperature variable and storage period of the PS cup. Both of these parameters have significance effect on styrene monomer migration.

It is also practical to use more sample of PS cups for each stimulant as to compare the result later on and verify the consistency of styrene migration from PS cup into food and beverages. Besides, contents of styrene monomer residual may also vary in different cups from different manufacturers. Consequently, by using PS cups from different manufacturers, it will further validate this research work.

## REFERENCES

- [1] International Life Science Institute, 2002, *Report on Packaging Material: 2. Polystyrene for Food Packaging Applications*, ILSI Europe Packaging Material Task Force, p 10
- [2] The Star Online, Friday February 1, 2008. 20 April 2008 <[www.thestar.com.my](http://www.thestar.com.my)>
- [3] International Life Science Institute, 2002, *Report on Packaging Material: 2. Polystyrene for Food Packaging Applications*, ILSI Europe Packaging Material Task Force, p 10
- [4] The Star Online- Thursday July 12, 2007. 20 April 2008 <[www.thestar.com.my](http://www.thestar.com.my)>
- [5] The University of Southern Mississippi, Department of Polymer Science. 27<sup>th</sup> May 2008 <[www.pslc.ws/mactest/styrene.htm](http://www.pslc.ws/mactest/styrene.htm)>
- [6] Robertson, G.L. 1992, *Food Packaging, Principles and Practices*, Marcel Dekker Inc. New York, USA, pp. 34-36
- [7] J.P.F. D'Mello 2003, *Food Safety: Contaminants and Toxin*, Oxford Cambridge, MA: CABI Publisher, pp 276-277
- [8] Wikipedia-Styrene. 9<sup>th</sup> February 2008 <<http://en.wikipedia.org/wiki/Styrene>>
- [9] Sheftel, Victor O. 2000, *Indirect Food Additives and Polymers Migration and Toxicology*, Boca Rota: Lewis Publisher, pp 142-145
- [10] Online in-print newsmagazine, Plastic and Your Health. 20 April 2008 <[www.thenewdominion.com](http://www.thenewdominion.com)>

- [11] Agency for Toxic Substances and Disease Registry (ATSDR), GA. 1992. *Toxicological Profile for Styrene*, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, p 3.
- [12] J.R. Withey, 1976. *Quantitative Analysis of Styrene Monomer in Polystyrene and Foods Including Some Preliminary Studies of the Uptake and Pharmacodynamics of the Monomer in Rats*. Environmental Health perspectives Vol. 17, pp. 125-153
- [13] International Life Science Institute, 2002, *Report on Packaging Material: 2. Polystyrene for Food Packaging Applications*, ILSI Europe Packaging Material Task Force, p 10
- [14] International Life Science Institute, 2002, *Report on Packaging Material: 2. Polystyrene for Food Packaging Applications*, ILSI Europe Packaging Material Task Force, p 10
- [15] Agency for Toxic Substances and Disease Registry ATSDR), GA. 1992, *Toxicological Profile on Styrene*, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, pp 150-153
- [16] Tawfik MS, Huyghebaert A. 15 July 1998, *Polystyrene Cups and Containers: Styrene Migration*, Department of Food Technology and Nutrition, Faculty of Agriculture and Applied Biological Sciences, Ghent, Belgium, p 9
- [17] Joint FAO/WHO Expert Committee on Food Additives, 2006, *Evaluation of Certain Food Contaminants*. Report Number 64, World Health Organization, Geneva, Switzerland
- [18] M. Ghazi-Khansari and M.Khaksar, July 2006, *Effects of Temperature and Time on Migration of Styrene Monomer from PS Cups into Milk*, Department of

Pharmacology, School of Medicine, Tehran University of Medical Sciences,  
Toxicology Letter, pp16-22

- [19] O.-G. Piringer and A. L. Baner 2000, *Plastic Packaging Materials for Food, Barrier Function, mass Transport, Quality Assurance and Legislation*, WILEY - VCH
- [20] Ahmad S. Bajahlan, Maqbool Ahmad, August 2006, *Leaching of styrene and other aromatic compounds in drinking water from PS bottles*, Environment Control Department, p 3

## **LIST OF APPENDICES**

**APPENDIX A: GANTT CHART**

**APPENDIX B: DATA FROM TGA ANALYSIS**

**APPENDIX C: FTIR DATA AND STANDARD ANALYSIS METHOD**

**APPENDIX D: DATA FROM GC-MS ANALYSIS**



## APPENDIX A

### GANTT CHART

Week Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<b>Activities/ milestones</b>														
Selection of Project Topic	x													
Preliminary Research Work		x												
Brainstorming			x											
Submission of Preliminary Report				x										
Survey Materials				x										
Seminar 1 (Optional)					x									
Project Work					x									
Prepare material (PS cup)					x									
Prepare stimulant sample					x									
Conduct Experiment						x								
Research Work							x							
Submission of Progress Report								x						
Seminar 2 Preparation									x					
Research Work									x					
Project work continues									x					
Data Gathering									x					
Submission of Interim Report Final Draft													x	
Preparation of Oral Presentation													x	
Oral Presentation														x

Figure: Milestone for the first semester of Final Year Project

## GANTT CHART

Details/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Work Continue														
-Practical/Laboratory Work														
Submission of Progress Report 1				x										
Project Work Continue														
-Practical/Laboratory Work														
Submission of Progress Report 2								x						
Project work continue														
-Practical/Laboratory Work														
Submission of Dissertation Final Draft												x		
Oral Presentation													x	
Submission of Project Dissertation (Hardbound)														x

Figure: Milestone for the second semester of Final Year Project

**APPENDIX B**  
**DATA FROM TGA ANALYSIS**

Table A-1: Readings from Thermogravimetric Analysis (TGA)

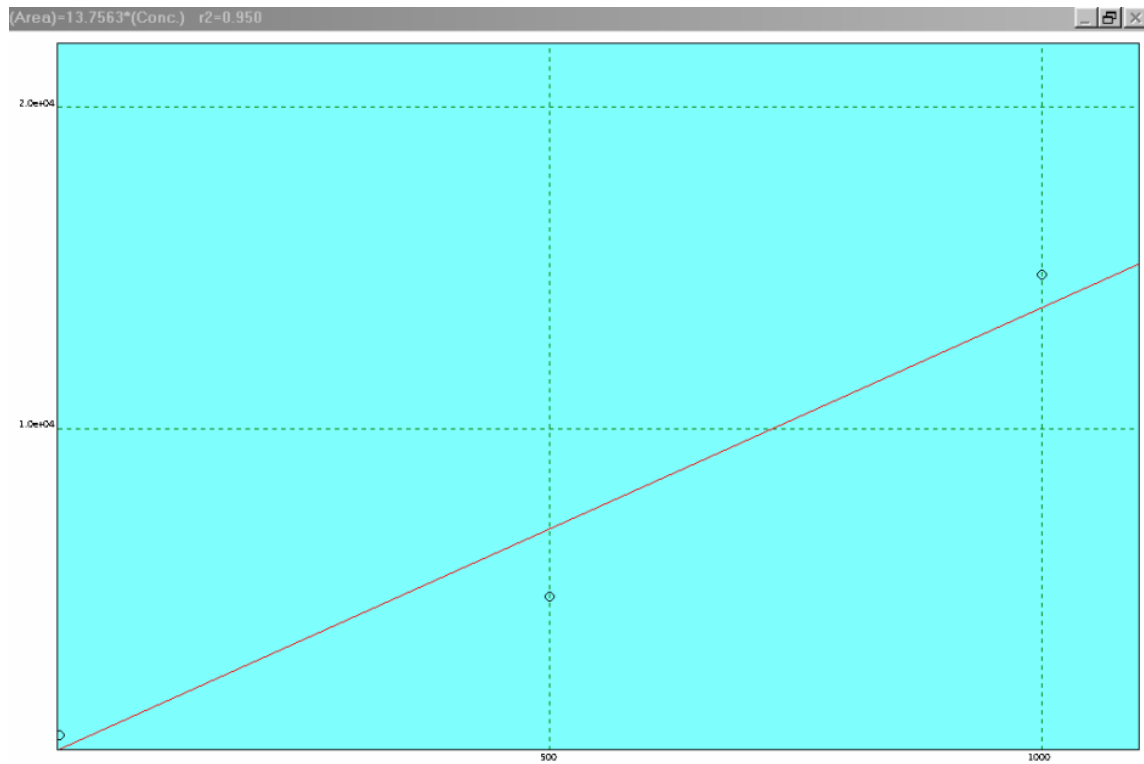
Temperature (°C)	Weight % (%)
25.003	99.973
35.022	99.976
45.002	99.9583
55.025	99.9348
65.289	99.8998
75.071	99.8743
85.145	99.8471
95.207	99.8173
105.064	99.7781
115.307	99.7448
125.243	99.6849
135.071	99.6679
145.187	99.7039
155.042	99.6701
165.059	99.4799
175.262	99.2403
185.083	99.1203
195.204	99.0501
205.202	98.9931
215.321	98.9449
225.098	98.9039
235.216	98.8599
245.304	98.8094

255.136	98.7557
265.132	98.685
275.226	98.6075
285.196	98.5106
295.022	98.3906
305.281	98.2269
315.182	97.9885
325.101	97.5999
335.255	96.9491
345.146	95.9505
355.058	94.4973
365.005	92.5405
375.25	89.7039
385.317	85.7793
395.113	80.6305
405.229	72.8512
415.025	61.9625
425.184	45.2608
435.044	23.4692
445.048	4.9124
455.346	0.0142

**APPENDIX C**  
**FTIR DATA AND STANDARD ANALYSIS METHOD**

**APPENDIX D**  
**DATA FROM GC-MS ANALYSIS**

## Calibration Curve from dilution of standard styrene monomer:



Level	En./Dis	Conc.	Average	Area1
1	enable	1	451	451
2	enable	500	4780	4780
3	enable	1000	14805	14805

\*To calculate concentration of styrene monomer in GC-MS spectrum,

$$\text{Concentration (ppb)} = \frac{\text{Area under the peak}}{13.7563}$$