



รายงานวิจัยฉบับสมบูรณ์

โครงการ : การแยกประเภทขยะพลาสติกด้วยวิธีฟอทโฟเทชั่น

โดย นางสาวสงบทิพย์ พงศ์สถาบดี และคณะ

30 มิถุนายน 2547

รายงานวิจัยฉบับสมบูรณ์

โครงการ : การแยกประเภทขยะพลาสติกด้วยวิธีฟอทโฟเทชั่น

คณะผู้วิจัย	สังกัด
1. ดร.สงบทิพย์ พงศ์สถาปติ	ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
2. นายณภัทร คุณาจิตพิมล	ภาควิชาการจัดการสิ่งแวดล้อม สาขาวิชาการจัดการสิ่งแวดล้อม
3. ศ.ดร.สมศักดิ์ ดำรงค์เลิศ	ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

การแยกประเภทขยะพลาสติกด้วยวิธีฟลูออโรเทชั่น

จุดประสงค์ของการทดลองครั้งนี้เพื่อแยกขยะพลาสติกผสมโดยแบ่งตามประเภทของพลาสติก โดยใช้วิธีผสมระหว่างความหนาแน่นและซีเล็คทีฟฟลูออเทชั่น ขยะพลาสติกผสมทั้งหกประเภท มีขนาด 0.3 ถึง 0.5 เซนติเมตร ประกอบด้วย ไฮเดนซิติ์ โพลีเอทิลีน (HDPE) โพลีโพรไพลีน (PP) โพลีไวนิล คลอไรด์ (PVC) โพลีสไตรีน (PS) โพลีเอทิลีน เทเรฟทาเท (PET) และอคริโรไนไตราย บิวทไดอิน สไตรีน (ABS) การแยกพลาสติกผสมด้วยความหนาแน่นทำโดยการปั่นขยะพลาสติกผสมอย่างทั่วถึงในสารละลาย และทิ้งพลาสติกไว้คืนที่เพื่อให้แน่ใจว่าขยะพลาสติกผสมนั้นแยกจากกันโดยสมบูรณ์ พลาสติกที่มีความหนาแน่นน้อยกว่าสารละลายจะลอยขึ้นสู่ผิวน้ำ ในขณะที่พลาสติกที่มีความหนาแน่นมากกว่าสารละลายจะจมอยู่ที่ก้นของสารละลาย การทดลองพบว่ามากกว่าร้อยละ 99 ของ PP ได้แยกจากขยะผสม PP และ HDPE โดยเอซิล แอลกอฮอล์ ร้อยละ 50 โดยปริมาตร PS และ ABS สามารถแยกจากขยะพลาสติกผสมโดยสมบูรณ์ด้วยร้อยละ 20 โดยน้ำหนัก ของสารละลาย แคลเซียม คลอไรด์ โดยที่ซีเล็คทีฟฟลูออเทชั่นเทคนิคจะทำการแยกขยะพลาสติกผสมที่ไม่สามารถแยกออกจากกันโดยสมบูรณ์ต่อจากวิธีแยกตามความหนาแน่น ซึ่งในการทดลองซีเล็คทีฟฟลูออเทชั่นเทคนิคนั้น ได้ทำการศึกษาอิทธิพลของเว็ดจ์เอเจนต์ ฟรอกเทอร์ พีเอช เวลาที่ใช้ในการทำปฏิกิริยา และอิเล็กโตรไลต์ ต่อการแยกขยะพลาสติก พบว่า PET แยกจากขยะพลาสติกผสม PET/PVC โดยได้ PET บริสุทธิ์ถึงร้อยละ 98.05 ในขณะที่ ร้อยละ 99.01 ของ PS สามารถแยกจากขยะพลาสติกผสม PS/ABS ในสถานะที่แตกต่างกัน

TITLE: FLOATING AND SELECTIVITY OF PLASTIC BY FROTH FLOTATION

KEY WORDS: PLASTICS WASTE SEPARATION/ SELECTIVE FROTH FLOTATION TECHNIQUE/ CONTACT ANGLE/ CALCIUM LINSULFONATE.

The aim of this research is to separate a mixed post-customer plastics waste based on type of plastics by using combining of gravity method and selective froth flotation. Analogous to gravity method, six mixed plastics wastes with 0.3 – 0.5 centimetre in size, composed of high density polyethylene (HDPE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), polyethylene terephthalate (PET) and acrylonitrile-butadiene-styrene copolymers (ABS) were stirred thoroughly in a medium solution and then left for four minutes to ensure complete separation. Plastics whose density less than that of medium solution was floated to the solution surface, while the one whose density was greater than that of medium solution was sunk to the bottom of the solution. The experimental results showed that more than 99% of PP (with commercial grade) could be separated from a mixture of PP and HDPE when using 50% by volume of ethyl alcohol acted as light medium solution. Mixture of PS and ABS could be separated completely from a mix of PS, ABS, PET and PVC by using 20% by weight calcium chloride aqueous solution. Consequently, selective flotation was then employed to separate these mixtures by which gravity method could not achieve. In this section, effect of wetting agent, frother, pH, conditioning time and electrolyte were studied. The results showed that PET could be separated from mixture of PET/PVC with 98.05 % of recovered PET when using 500 ppm Calcium lignosulfonate (CaLS) as wetting agent, 0.1% CaCl_2 as electrolyte, 0.02 ml MIBC as a frother, at pH 11 and conditioning time 3 minutes. It was found that 99.01% of PS was separated from the mixture of PS/ABS as by using different condition.

ACKNOWLEDGEMENT

First of all, I wish to express my sincere appreciation to Prof. Dr. Somsak DAMRONGLERD, my mentor, for his encouragement, giving me the good advices. I would like also to express my thank to Mr.Napatr KUNACHITPIMOL for serving as one of my research team.

Acknowledgement goes to TRF and MUA for financial support and giving me a good chance to do this research. Additional acknowledges furnishing of facilities and equipments for this research from department of chemical technology, faculty of science, Chulalongkorn University (CHEM-TECH). I also acknowledge department of material science, faculty of science, Chulalongkorn University for providing contact angle measurement.

Last but not least, I thank to all my friends and whoever supported and involved in this research that I did not name.

EXECUTIVE SUMMARY

สัญญาเลขที่ MRG4680087

โครงการ : การแยกประเภทขยะพลาสติกด้วยวิธีฟลอย์โฟเทชั่น

ชื่อโครงการ (ภาษาไทย) : การแยกประเภทขยะพลาสติกด้วยวิธีฟลอย์โฟเทชั่น
(ภาษาอังกฤษ): Floating and Selectivity of Plastic by Froth Flotation

ชื่อหัวหน้าโครงการวิจัยผู้รับทุน (ภาษาไทย) : นางสาวสงบทิพย์ พงศ์สถาบดี
(ภาษาอังกฤษ): Ms. Sangobtip PONGSTABODEE

หน่วยงาน: ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ระยะเวลาดำเนินงาน 1 ปี (1 กรกฎาคม 2546 ถึง 30 มิถุนายน 2547)

เวลาทำงานวิจัยในโครงการนี้โดยประมาณสัปดาห์ละ 20 ชั่วโมง

ความสำคัญและที่มาของปัญหา

ขยะพลาสติกในเมืองไทยมีปริมาณเพิ่มขึ้นเป็นจำนวนมาก เนื่องจากความนิยมของประชาชนต่อการใช้วัสดุที่ทำมาจากพลาสติก การกำจัดขยะพลาสติกมีวิธีการที่แพร่หลายอยู่ 3 วิธี คือ การฝังกลบ การเผา การรีไซเคิล ซึ่งแต่ละวิธีก็มีข้อเสียดังนี้ การฝังกลบต้องการพื้นที่มากและตัวพลาสติกเองมีอายุการย่อยสลายนานมาก ๆ บางชนิดเกือบร้อยปี ส่วนการเผาก็ทำให้เกิดมลพิษทางอากาศและยังเสียค่าใช้จ่ายด้านเชื้อเพลิงที่ใช้ในการเผา พลังงานที่ได้จากการเผาก็ไม่มากพอที่จะนำกลับมาใช้ประโยชน์ การรีไซเคิลพลาสติกมักได้ผลิตภัณฑ์ที่มีคุณภาพต่ำลงเนื่องจากไม่มีการแยกชนิดของขยะพลาสติก เพื่อเพิ่มคุณค่าและคุณภาพของพลาสติกรีไซเคิลจึงจำเป็นต้องแยกประเภทของพลาสติกก่อนการรีไซเคิล ดังนั้นงานวิจัยนี้จึงได้ประยุกต์เทคนิคฟลอย์โฟเทชั่นในการแยกขยะพลาสติกผสมออกตามชนิดของพลาสติกนั้น ๆ หลักการของเทคนิคฟลอย์โฟเทชั่นคือการเป่าอากาศเข้าสู่ระบบ เมื่อฟองอากาศไปเกาะที่วัสดุใด ก็จะทำให้เกิดแรงลอยตัวหรือแรงพยุง ซึ่งวัสดุต่าง ๆ ก็จะทำให้ค่าแรงลอยตัวที่ต่างกัน นอกจากนี้วัสดุต่าง ๆ ก็มีความสามารถในการเกาะกับฟองอากาศต่างกันอีกด้วย ดังนั้นวิธีนี้สามารถแยกพลาสติกตามประเภทของพลาสติกให้มีความบริสุทธิ์ในระดับที่สามารถนำกลับมาใช้ประโยชน์ได้มากขึ้น และยังคงคุณสมบัติของพลาสติกไว้ตามเดิม งานวิจัยนี้ยังใช้เป็นแนวทางในการพัฒนาระบบการแยกและการนำกลับมาใช้ใหม่ของวัสดุชนิดต่าง ๆ

วัตถุประสงค์

1. เพื่อหาแนวทางในการแยกชนิดของขยะพลาสติกได้อย่างมีประสิทธิภาพ
2. หาสภาพที่เหมาะสมในการแยกขยะพลาสติกโดยวิธีฟลอตโฟเทชั่น

สรุปผลการทำงานวิจัย

Six common post-consumer plastics wastes namely PET, HDPE, PVC, PP, PS and ABS selected for this study were hydrophobic in nature. PP and HDPE could be separated from mixtures plastics by density separation but the other plastics could not because of their densities and surface energy limitation.

It was possible to separate PET from PVC through selective flotation by using calcium lignosulfonate as a wetting agent and methyl isopropyl carbinol as frothing agent. Similarly, mixture of ABS and PS could also be separated from each other by selective flotation. CaLS can dramatically reduce liquid surface tension. The depressant effects of wetting agent on the plastics are results of the reduced surface tension and adsorption on the plastics surface. The CaLS molecules adsorbed on the plastics surface expose some their polar groups oriented toward the aqueous phase, hence making the plastics surface hydrophilic. Electrostatic interaction and van-der-Waals force are the main interactions between CaLS and plastics surfaces.

However, ABS/PS had more special parameter, ethyl alcohol, for modifying density of medium. The depressing effect of CaLS on plastics was attributed mainly to its adsorption on plastics surface. The CaLS molecules absorbed on plastics surface expose the polar groups adjusted towards the liquid phase, hence making the plastics surface hydrophilic. Other very important parameter was conditioning time of the plastics mixture. Longer conditioning time made all plastics too hydrophilic, which was not desire. Because successful plastics separation by selective flotation technique necessitated made each plastics to hydrophilic state but another maintained in a hydrophobic state. Therefore, hydrophobic plastics floated to the surface of the medium but hydrophilic plastics remained in the bottom of the flotation column.

However, higher flotation column separation reduced the bond between plastics surface and air bubbles. This means that hydrophobic plastics; should be floated to top of the column, could not attach the air bubble through the surface of the medium solution and fall down to the bottom. Hence, hydrophobic plastics still contaminated with hydrophilic plastics.

In **Figure 1**, the purposed flow chart in this study is presented. The summaries of the experiment were shown below:

- i) PP and HDPE were first separated from the plastics mixtures by 50 %v/v LMS.

ii) While, PET, PVC, ABS and PS still mixed together. PET and PVC were separated from ABS and PS by 20 %w/v DMS.

iii) Mixture of PET and PVC was separated individually by 500 mg/l CaLS at pH 11, conditioning time 3 minutes, 0.1 %w/v CaCl_2 and 0.02 ml of MIBC.

iv) Furthermore, PS was separated from ABS by 200 mg/l CaLS at pH 7 conditioning time 4 minutes and 0.1 %w/v CaCl_2 . These results of sink-float method and selective flotation separation were also summarised in **Figure 1**.

Clean, pure plastics, which was separated from mixed post-consume plastics wastes were the suitable raw materials to recycling plastics. Thus, all plastics wastes must be separated prior to recycling. In generally, there are many types of plastics that used in many applications in daily life so just six plastics separation method in this work is not enough. Furthermore, there are other wetting agents that can be used to separate plastics wastes. So in the future work, CaLS and types of plastics should be change to the others for covering the all plastics wastes.

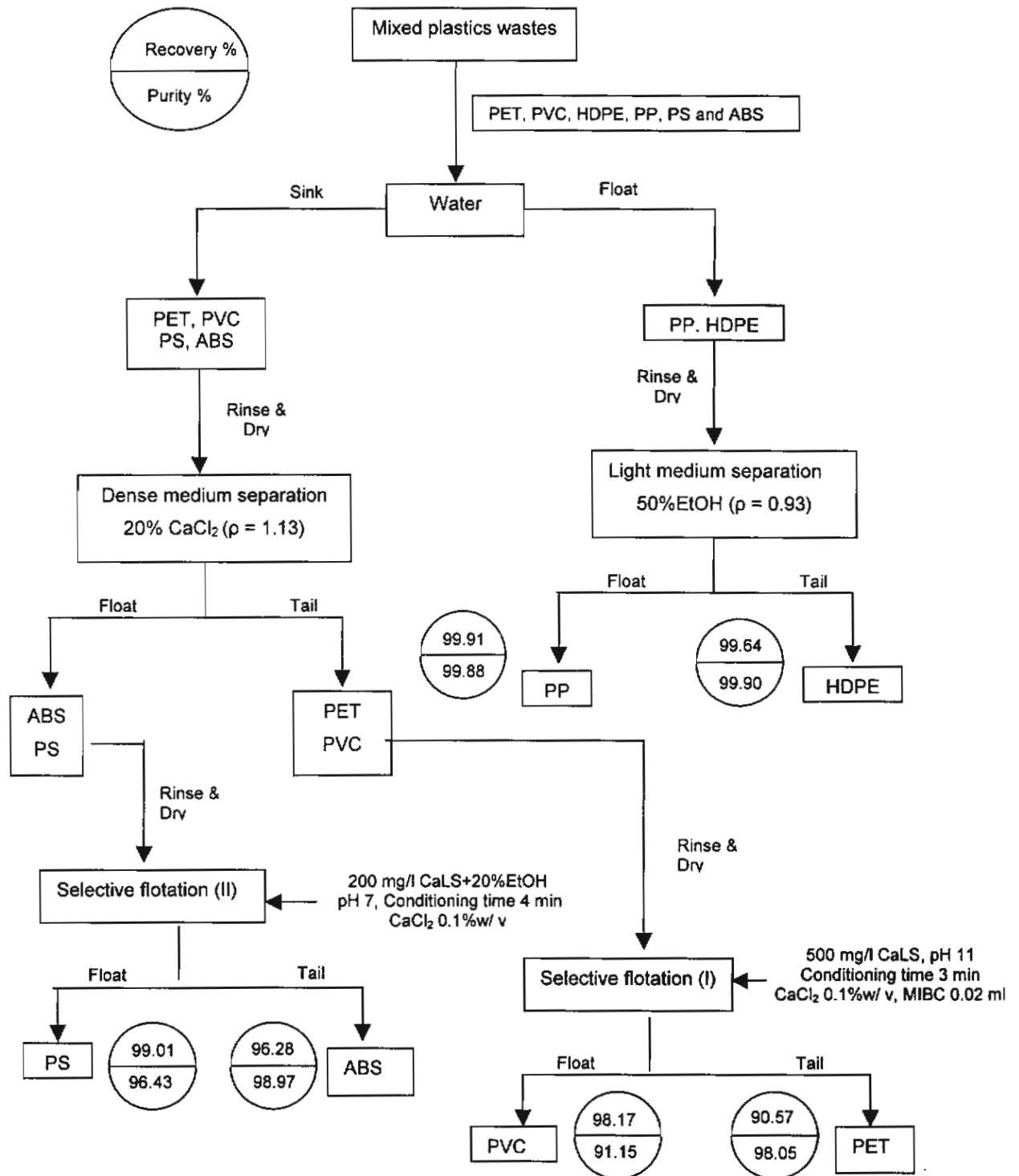


Figure 1 Proposed flow chart for separation of plastics mixtures by sink-float method and selective flotation technique

ผลงาน/หัวข้อเรื่องที่คาดว่าจะตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ขณะนี้กำลังดำเนินการเตรียมเอกสารเพื่อตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ชื่อเรื่องที่คาดว่าจะตีพิมพ์

Floating and Selectivity of Plastic by Froth Flotation

ชื่อวารสารที่คาดว่าจะตีพิมพ์

Sep Purif Technol (IF = 0.552)

CONTENTS

	Page
ABSTRACT (Thai).....	iv
ABSTRACT (English).....	v
ACKNOWLEDGEMENTS.....	vi
EXECUTIVE SUMMARY.....	vii
CONTENTS.....	xii
LIST OF TABLES.....	xiv
LIST OF FIGURES.....	xv
 CHAPTER I Introduction	 1
1.1 Introduction and motivation.....	1
1.2 Objectives.....	2
 CHAPTER II Theoretical background and literature reviews.....	 3
2.1 Plastics.....	3
2.2 Common plastics.....	5
2.3 Plastics wastes and plastics wastes management.....	7
2.4 Recycling trend in Thailand.....	12
2.5 Selective flotation.....	12
2.6 Related works.....	13
 CHAPTER III Methodology.....	 15
3.1 Plastics samples.....	15
3.2 Chemical reagents.....	16
3.2.1 Sink-float separation.....	16
3.2.2 Selective flotation test.....	16
3.3 Experiment methods.....	16
3.3.1 Sink-float separation.....	16
3.3.2 Selective flotation test.....	17
3.4 Contact angle measurement.....	18
 CHAPTER IV Results and discussions.....	 20
4.1 Sink-Float method.....	20
4.1.1 Dense medium solution.....	21
4.1.2 Light medium solution.....	24

CONTENTS (Cont)

	Page
4.2 Selective flotation technique.....	25
4.2.1 PET/PVC.....	25
4.2.1.1 The effect of treatment with CaLS wetting agent	25
and pH on the floatability	
4.2.1.2 The effect of conditioning time on the floatability of plastics.....	27
4.2.1.3 The effect of varying the concentration of.....	28
electrolyte on the floatability of plastics	
4.2.1.4 The effect of frothers and their concentrations....	30
on the floatability of plastics	
4.2.1.5 The effect of height of flotation cell on.....	32
the floatability of plastics	
4.2.2 PS/ABS.....	32
4.2.2.1 The effect of treatment with CaLS wetting agent	32
and pH on the floatability	
4.2.2.2 The effect of conditioning time on the floatability of plastics.....	34
4.2.2.3 The effect of varying the concentration of.....	35
electrolyte on the floatability of plastics	
4.2.2.4 The effect of frothers and their concentrations....	36
on the floatability of plastics	
4.2.2.5 The effect of height of flotation cell on.....	38
the floatability of plastics	
4.3 Contact angle measurement.....	39
4.4 Assessment of application of chemical conditioning method in.....	43
plastics flotation	
 CHAPTER V Conclusions.....	 44
 REFERENCES.....	 47

LIST OF TABLES

Table	Page
1.1 Price of some common plastics resins in July 2002 in Thailand.....	2
2.1 Data on plastics processing industry in Asian Regions (other than China).....	6
2.2 SPI's voluntary plastics container coding system.....	10
4.1 Density of plastics.....	23
4.2 Densities of calcium chloride aqueous solution (DMS) in varied concentrations.....	23
4.3 Densities of ethyl alcohol solution (LMS) in varied concentrations.....	23
4.4 Flotation experiments results according to conditioning time..... at 500 mg/l CaLS, pH 11	28
4.5 Flotation experiments results according to height of flotation column.....	32
4.6 Flotation experiment results according to height of flotation column.....	38
4.7 The comparison of plastics recovery and recovered plastics purity.....	38
4.8 Contact angles of plastics with water.....	39

LIST OF FIGURES

Figure	Page
2.1 The plastics consumption in 1999.....	6
2.2 Percent by weight of solid wastes in MSW, Bangkok 2000.....	7
2.3 Density of common plastics.....	11
3.1 Schematic a configuration of each plastics	15
3.2 Flotation column.....	18
3.3 Diagram of experiment procedure.....	19
4.1 Plastics separation by using water.....	20
4.2 Plastics separation by using dense medium solution.....	21
4.3 The floatability of plastics in the presence of DMS.....	22
4.4 The floatability of plastics in the presence of ethyl alcohol solution (LMS).....	24
4.5 Dependence of the floatability of PET and PVC on the varied.....	26
CaLS concentration at pH 7	
4.6 Dependence of the floatability of PET and PVC on the varied pH at 500 mg/l CaLS....	26
4.7 Floatability and purity of PET and PVC on the varied time at 500 mg/l CaLS, pH 11....	27
4.8 The effect of cation on the floatability and purity of PET.....	29
(using 500 mg/l CaLS, pH 11)	
4.9 The effect of cation on the floatability and purity of PVC.....	29
(using 500 mg/l CaLS, pH 11)	
4.10 The role of calcium in the adsorption mechanism of lignosulfonate.....	30
on plastics surface	
4.11 The concentrations of frother reagents (MIBC and terpineol) as function of.....	31
separation PET and PVC	
4.12 Dependence of the floatability of ABS and PS on the varied.....	33
CaLS concentration at pH 7	
4.13 Dependence of the floatability of ABS and PS on the varied pH at 200 mg/l CaLS....	34
4.14 Floatability and purity of ABS and PS on the varied time at 200 mg/l CaLS, pH 7....	35
4.15 The effect of cation on the floatability and purity of ABS and PS	36
(using 200 mg/l, pH 7 and 4 minutes conditioning time)	
4.16 The concentration of MIBC as function of ABS/PS separation	37
4.17 The concentration of terpineol as function of ABS/PS separation.....	37
4.18 Contact angle of PET and PVC with deferent concentrations of CaLS and pH.....	40
4.19 Contact angle of PS and ABS with deferent concentrations of CaLS and pH.....	41
4.20 Contact angle of plastics with deferent concentrations of CaCl ₂	42

LIST OF FIGURES (Cont)

Figure	Page
5.1 Proposed flow chart for separation of plastics from mixtures by..... combination of sink-float method and selective flotation technique	46

CHAPTER I

INTRODUCTION

1.1 Introduction and motivation

Environmental protection has been a serious concern in the civilized nations of the world. It has been known that lack of an appropriate waste disposal and a huge of consumers lead to the environmental deterioration. Plastics wastes are more and more generated by industries and municipalities each day. The statistics shows that plastics waste in municipal solid wastes (MSW) in Thailand reached 7.7 thousand tons/day in the year 2000 that increasing 2.4 thousand tons/day from 1998 (Pollution Control Department; PCD, 2004). The increasing of plastics waste has a negative impact on the management of solid wastes. Usually, there are three existing techniques for plastics disposal are landfilling, incineration and recycle. All of these still have their own-disadvantage. Plastics disposal by landfill needs a vast area and plastics themselves need very long time to be degraded. Moreover, it is not worthy to dispose the plastics wastes when no reaching their lifetime. In case of incineration, air pollution, such as dioxin, which is a hazardous material, is produced and released to the atmosphere (National Metal and Materials Technology Center; MTEC, 1998). Nevertheless, incineration gives pretty amounts of heat energy but it still does not enough to produce electricity.

Recycling is an alternative way to manage the plastics waste. Plastics waste recycling is a method of reducing the quantity of net discharges of MSW. Furthermore, plastics recycling also offers a potential to generate demonstrable save in fossil fuel consumption because the recycled plastics required less energy than that consumed in the production of the same resins from virgin feedstock (Curlee, T.R. *et al.*, 1991). Therefore plastics waste recycling conserves both virgin material and energy consumption. In addition, the plastics waste recycling also provides a comparatively simple way to make a substantial reduction in the overall volume of MSW. Recycling plastics combines with four phases activities, namely collection, separation, processing (manufacturing) and marketing. When plastics with different types are mixed and then recycled together; it is found that the quality of the recycled mixed plastics is worse than that of those virgin one. For instance, as a little as 1 ppm of PVC in PET can discolour PET. PET will be hazy (Ehrig, R.J., 1992). Therefore, cost of the recycled mixed plastics is significantly lower. From above, plastics wastes must be separated based on type of plastics used before recycling. Thus, individual separation of the mixed plastics waste is an important activity in recycling plastics process in order to keep their

properties and value. Price of some common plastics virgin plastics resins was reported by Thai Plastics Industries Association in July 2002 (**Table 1.1**). These led authors to investigate in mixed plastics waste separation by combination of sink-float method and selective flotation technique.

Table 1.1 Price of some common plastics resins in July 2002 in Thailand
(Thai Plastics Industries Association, 2002)

Plastics resins	Price (Baht/kg)
PVC injection grade	41.00
LDPE film grade	26.00 – 28.00
LDPE injection grade	27.00 – 29.00
HDPE film grade	24.00 – 26.00
PP film grade	25.00 – 26.50
PP yarn grade	24.00 – 25.00
HIPs	31.00 – 32.00
ABS	39.00 – 42.00
GP-PS	30.00 – 31.00
PC	130.00
PET	37.00
PU	228.00

1.2 Objectives

The main objective was to individually separate a mixture of plastics waste by combining between sink-float separation and selective flotation technique. An optimal condition for separating each plastics from a mixture was also considered.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Plastics

Plastics (Greek: *plastein* = to form, to shape) are commercially versatile materials that are based on polymers or prepolymer: long chain carbon-based organic molecule. These chains are made up of repeating fundamental molecular elements, or monomers. The name "Plastics" refers to their easy processability and shaping (Hans, G.E., 1993) or a material that contains as an essential ingredient organic substance of large molecular weight, is solid in its finished state and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow (ASTM D883-54T). Early plastics and their polymers and prepolymers resembled natural resin. These natural resins are organic solids that break with a conchoidal fracture in contrast to the planar surfaces created upon the breaking of gums and waxes. People have been using natural organic polymers for centuries in the form of waxes and shellacs, as well as fabrics and ropes, which are based on a plant polymer named cellulose.

Historically, plastics were usually classified into two types according to the heat response of plastics (physical or chemical hardening processes) long before there was a realization of chemical nature of this material. This group of plastics is based on the physical changes that occur when plastics are subjected to heat and cool. Two types of plastics in this group are:

Thermoplastics yield solid materials by simply cooling a polymer melt (a physical process); they soften upon heating. They are normally composed of fairly high molar mass molecules since it is only above a certain molar mass that many physical properties become effectively molar mass independent. Examples are melting temperatures and moduli of elasticity. Other properties increase however with increasing molar mass, e.g., melts viscosities.

Thermosetting resin, on the other hand, harden through chemical cross-linking reactions between polymer molecules and become "thermosets" because their shapes and properties are "set" by this process. Upon heating, they do not soften but decompose chemically. The shaping of thermoplastics is thus a reversible process: the same material can be melted and process again. Thermosets cannot remelted and reshaped; their formation is irreversible.

However, thermoplastics and thermosets have been further subdivided on a cost-property performance into:

Commodity thermoplastics are manufactured in great amounts because they are less costly. The commodity plastics also have lower physical properties and are used in applications with less demanding performance requirement; hence the terms bulk plastics, volume plastics or standard plastics. They include poly(vinyl chloride)-PVC, poly(ethylene)s (high density, low density and very low density)- HDPE, LDPE, LLDPE, isotactic poly(propylene)-PP, and standard poly(styrene)-PS.

Engineering plastics (technical plastics, technoplastics) are in general thermoplastics (ETPs) that process improved mechanical properties compared to commodity plastics; some thermosets may also classify as engineering plastics. They have load-bearing characteristics that permit them to be used in the same manner as melts and ceramics. Such improved properties may be higher moduli of elasticity, smaller and cold flows, higher impact strengths, etc. Engineering plastics are also often defined as those thermoplastics that maintain dimensional stability and most mechanical properties above 100 °C or below 0 °C. Engineering plastics comprise poly(ethylene terephthalate)-PET, poly(butylene terephthalate)-PBT, polyamides-PA, polycarbonates-PC, some modified poly(styrene)s such as styrene/acrylonitrile (SAN) and acrylonitrile/butadiene/styrene (ABS) copolymers and high-impact poly(styrene)s-SB, as well as various blend such as poly(phenylene oxide)-poly(styrene) and polycarbonate-ABS.

High-performance plastics, on the other hand, are engineering plastics with even more improved mechanical properties. They comprise liquid crystalline polymers, various polyetherketones, difference polysulfones, poly(phenylene sulfide), various polyamides, etc.

Functional plastics have only very specific use. Poly(ethylene-co-vinyl alcohol) with a high content of vinyl alcohol units is a functional plastics that is only used as a barrier resin in packaging. Other function plastics are employed in optoelectronics, as piezoelectronic materials.

Fluoroplastics are specialty plastics because of their surface properties. They comprise poly(tetrafluoroethylene)-PTFE/Teflon, poly(chlorotrifluoroethylene)-PCTFE, poly(vinylidene fluoride)-PVDF and many other fluorinated polymer.

2.2 Common plastics

In modern world, plastics have become a universal material and played important role in many applications, used for everything from throwaway bags to combat aircraft wings. Plastics are cheap, lightweight, strong, often attractive, and can be synthesized with a wide range of properties. So the global production of plastics has grown exponentially over recent years and therefore correlates quite well with population growth. Presently, the use of plastics in consumer goods is relatively more prevalent in the developed countries. In fact the per capita consumption of plastics worldwide correlates surprisingly well with the per capita gross national product (GNP) of the country. In affluent countries such as Japan and in Western Europe plastics consumption can be as high as 90 Kg/person-year as opposed to less than 4.5 Kg/person-year in the least developed countries (Kim, U.Y. *et al.*, 1995) while, Thailand plastics consumption was about 28 Kg/person-year (The Federal of Thai Industry; FTI, 2001). In Thailand the demand for commodity plastics continually grew in the 1990s and during the recent period of 1994 – 2000, the consumption of plastics increased at compound growth rate of 31 – 63 %, depending on the application area (FTI, 2001). Packaging applications are particular interest from environmental standpoint because of the high visibility of packaging in MSW and in urban litter and account for about a quarter of the U.S. demand for thermoplastics (Anthony, L.A. *et al.*, 2003 and Ehrig, R.J. *et al.*, 1992). The domestic growth rate for plastics in recent year has been in bottle and container applications of HDPE, fibre and closure application of PP and in PVC.

A comprehensive introduction of common plastics above show that it is only those plastics that are used in high enough volume in common applications, those interact significantly and visibly with the environment. This is particular true of solid-waste related issues where attention has often focused on polystyrene and polyolefins^a packaging materials. Also, the magnitude of environmental impacts generally increases with the worldwide production volume of a material. For the present purpose “common” plastics include the high-volume commodity resins. In Thailand, polyethylene is the highest consumed for plastics that comprised 43%. Next are polypropylene, poly(vinyl alcohol), polystyrene, thermoplastics polyester respectively (**Figure 2.1**).

^a Polyolefins are PE and PP.

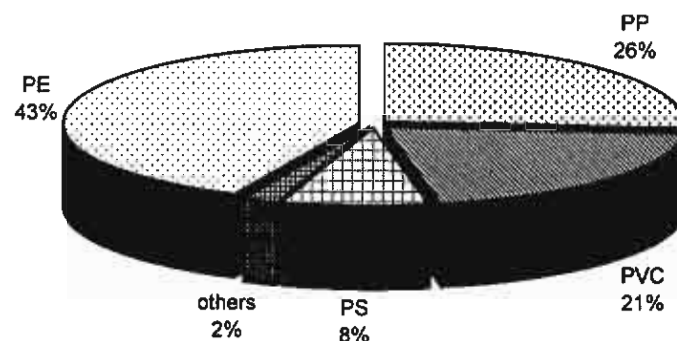


Figure 2.1. The plastics consumption in 1999 (FTI, 2001)

Table 2.1 summarises the plastics industry in different Asian countries; the data is approximate but adequate to yield some idea of the magnitude of the industry. Japan is the largest demand for plastics while, Thailand is the froth that demands two million tones for plastics.

Table 2.1 Data on plastics processing industry in Asian Regions (other than China)
(Anthony, L.A. *et al.*, 2003)

Country	Plastics Processing Capacity (million tons)	GDP (billion USD)	Plastics Processing Capacity (million tons)	Plastics Processing Capacity (million tons)
Hong Kong ^a	27.2	220	7	1 million +
Malaysia	21	215	1	85,000
Taiwan ^a	22	362	3	150,000
South Korea	47	580	4 ^b	100,000
Thailand	60	369	2 ^b	—
Japan	127	3913	9	458,000
Singapore	4	92	0.3	13,000

^a Data for Hong Kong and Taiwan have been separately compiled although they are part of China

^b 1997 Data. Table was compiled from data of Kim, U.Y. *et al.*, 1995.

2.3 Plastics wastes and plastics wastes management

At the end of the 19th century the industrial revolution saw the rise of the world of consumers. Not only did the air and water get more and more polluted but also the earth itself became more polluted with the generation of non-biodegradable solid waste. The increase in population and urbanisation was also largely responsible for the increase in solid waste.

Plastics play an important role in almost every aspect of our lives. Plastics are used to manufacture everyday products such as beverage containers, household items, and furniture. The widespread use of this valuable material demands proper management of used plastics, as they have become a larger part of the municipal solid waste (MSW) stream in recent decades. The statistics show that plastics waste in Thailand's MSW reached 2.8 million tons in 2000 increasing 47% from 1999 (PCD, 2004). The proportion of plastics comprised 17% of total MSW is the second most of wastes next to organic waste only (**Figure 2.2**). Plastics are so versatile in use that their impacts on the environment are extremely wide ranging. However, the along with a growth in the use, a country-wide network for collection of plastic waste through rag pickers, waste collectors and waste dealers and recycling enterprises has sprung all over the country over the last decade.

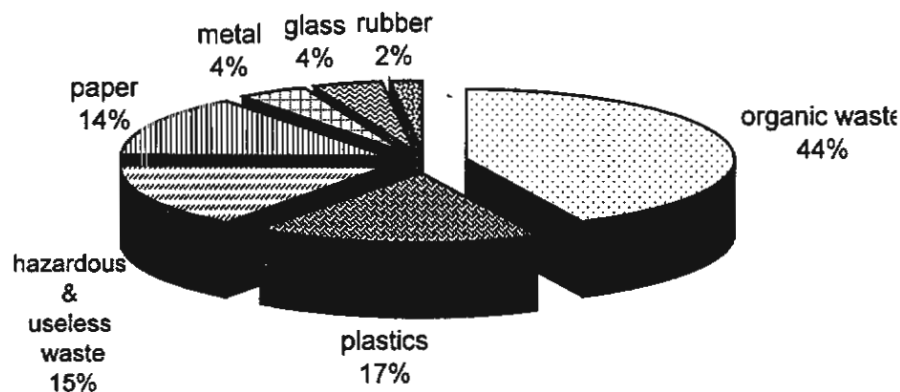


Figure 2.2 Percent by weight of solid wastes in MSW, Bangkok 2000 (PCD, 2004)

Careless disposal of plastic bags chokes drains, blocks the porosity of the soil and causes problems for groundwater recharge. Plastics disturb the soil microbe activity, and once ingested, can kill animals. Plastics bags can also contaminate foodstuffs due to leaching of toxic dyes and transfer of pathogens. In fact, only approximately 0.4 million tons or 16% of the plastics waste generated in Thailand is collected and segregated to be recycled (PCD, 2004). The rest remains strewn on the ground, littered around in open drains, or in unmanaged garbage dumps. Though only a small percentage lies strewn, this portion should be concerned as well because of its extensive damage to the environment.

In Thailand, the usual plastics managements are landfilling and incineration, however, both of them have own advantage and disadvantage. Landfilling is likely to remain the dominant solid waste disposal near the future. Once dispose in a landfill, very little deterioration of the waste is expected. Even the rapidly biodegradable materials such as paper and yard waste fractions persist for long periods of time in landfills due to the absence of enough moisture and oxygen needed to support a biotic environment within the fill (Vasuki, N.C., 1988). This is particularly true food or yard waste contained in plastics bags. Certainly, the plastics fraction does not break down significantly in these conditions. This lack of deterioration is not undesirable; as no polluting leachates or flammable gases are produced in any significant volumes and the fill remains stable as the volume of compacted waste remain the same. The available landfill capacity in Thailand is rapidly decreasing. Hence, the generally perceived undesirability of plastics in the MSW stream stems from the argument that since plastics do not biodegradable in landfill environment they do not yield their occupied volume for additional disposal of waste. The real issue relating to plastics waste in landfill is that represents a valuable resource discharge well before the end of its useful lifetime (or even after only a single use). The actual cost the waste plastics can only be appreciated if all the natural resource and environmental cost invested in its production are correctly taken into account. Rather than burying these valuable raw materials, the landfills should perhaps be thought of as temporary repositories of durable plastics waste for future recycling or conversion into useful energy.

Incineration of MSW allows the recovery of energy from the fuel gases formed in the process. This energy might be used to generate steam and consequently convert into electricity. Incineration, however, is not always a particular clean process and the plastics fraction in the waste has been blamed for compounding the air pollution impact. Specifically, the production of hydrogen chloride in burning PVC, the contribution of the chlorine from PVC to the formation of dioxins (Anthony L.A., 2003 and MTEC, 1998) and the influence of plastics on metal content of the incinerator ash have been pointed out.

According to section 1.1 of Chapter I, most plastics can be recycled, but due to the difficulty in collecting, sorting, cleaning and reprocessing. Plastics collected for recycling must first be separated into polymer types. Because only using clean, homogeneous resins can produce the highest-quality recycled plastic products in the existing secondary process (material recycling) and high-value chemical products in the existing feedstock recycling. Then, an effective separation of mixed plastics waste is necessary. To help identify different plastics, manufacturers stamp a Plastics Identification Code on their products. This code is a number inside a triangle with chasing arrows. These codes only to identify the product and do not indicate that the product can be recycled. The codes for the six most common plastics are shown in the **Table 2.2**. The codes help recycling contractors to sort the plastics. Bales of different types of plastics are then returned to factories for reprocessing. To reprocess the plastics:

- Large contaminants are manually removed.
- The plastics are either shredded, chopped or ground and then washed to remove further contaminants.
- The material is dried and formed into pellets or powder, ready for remaking into new plastic products.

Although several separation technologies, including manual sorting, gravity separation, electrostatic separation and flotation, etc. can be applied to separate mixed plastics waste, they have their limitations. Some available techniques for plastics separation will be described below.

- *Manual sorting* of plastics involves identifying various characteristics of containers by persons with a trained eye as the container travel along a moving conveyer. Manual sorting of post-consumer polymers, however, is both labour intensive and ineffective. Increasing labour costs are making manual sorting economically unviable. Furthermore, the resulting product, which is costly to produce, generally only finds limited application in low-value products, due to the possibility of human error during the sorting operation.

Table 2.2 ^aSPI's voluntary plastics container coding system

Recycling Identification Code	Plastic Material	Characteristics	Source: Recycle for Plastic Waste	Source: Recycle for Plastic Waste Recycling Centre
 PETE	Polyethylene terephthalate (PET)	Clear, tough plastics, may be used as a fibre.	Soft drink and mineral water bottles, filling for sleeping bags and pillows, textile fibres.	Soft drink bottles, (multi-and mono- layer) detergent bottles, clear film for packaging, carpet fibres, fleecy jackets.
 HDPE	High-density polyethylene (HDPE)	Very common plastics, usually white or coloured.	Crinkly shopping bags, freezer bags, milk and cream bottles, bottles for shampoo and cleaners, milk crates.	Compost bins, detergent bottles, crates, mobile rubbish bins, agricultural pipes, pallets, kerbside recycling crates.
 PVC	Polyvinyl chloride (PVC)	Hard, rigid plastics may be clear.	Clear cordial and juice bottles, blister packs, plumbing pipes and fittings.	Detergent bottles, tiles, plumbing pipefitting.
 LDPE	Low-density polyethylene (LDPE)	Soft, flexible plastics.	Lids of ice-cream containers, garbage bags, garbage bins, black plastics sheet.	Film for builders, industry packaging and plant nurseries, bags.
 PP	Polypropylene (PP)	Hard, but flexible plastics many uses.	Ice-cream containers, potato crisp bags, drinking straws, hinged lunch boxes.	Compost bins, kerbside-recycling crates, worm factories.
 PS	Polystyrene (PS)	Rigid, brittle plastics. May be clear and glassy.	Yoghurt containers, plastics cutlery, imitation crystal 'glassware'.	Clothes pegs, coat hangers, office accessories, spools, rulers, video/CD boxes.
 OTHER	Others	Includes all other plastics, including acrylic, ABS and nylon.		

^a SPI is The Society of the Plastics Industry, Inc.

➤ *Sink-float separation* is usually accomplished with a fluid medium that has a density, which is intermediate to that of the plastics being separated. Plastics less dense than the medium will float and the heavier will sink. A major limitation of this method is that many plastics have virtually equivalent or fairly similar densities (**Figure 2.3**). Typical fluids that are used for the medium are water, water/methanol mixtures (to sort plastics with specific gravities less than unity such as polyolefins), saline solutions and zinc chloride solutions (for plastics with specific gravities greater than unity). The sink-float method is widely used to separate polyolefins from PET and PVC using water as the process medium. Mixed polyolefins are notoriously difficult to separate by sink-float method because of the small gap between their densities. For example, the density gap between LDPE and HDPE can be only 0.001 g/cm^3 , while that between HDPE and PP is 0.03 g/cm^3 . A further problem with this method is that it can be slow, difficult to control and may yield low-purity product streams. The density of the aqueous solution can be difficult to control precisely, due to variations in the ambient temperature. Along with this, the evaporation of binary solutions leads to changes in composition and thus solution density. Surface tension can affect also plague sink-float process. Moreover, the agglomeration of different flakes can force a lighter particle to sink when flanked and clustered by heavier particles. Other aspects of this process may include intensive washing steps to detach dirt adherent labels. A disadvantage of such sink-float method is that considerable quantities of wastewater are generated, which requires special treatment.

- *Flotation* process has been devised to separate commingled plastics on the basis of different hydrophobicity. The plastics flakes are placed in an aqueous medium, which is agitated by mechanical stirring or by bubbling air through the bottle of mixture. Flotation technique can be concluded that the flotation of plastics is fairly flexible technique and could prove to be a useful process for separation of mixture of several different type of plastics. Hence, this technique is chosen to separate the mixed plastics in this work. The more details will be specified in next section.

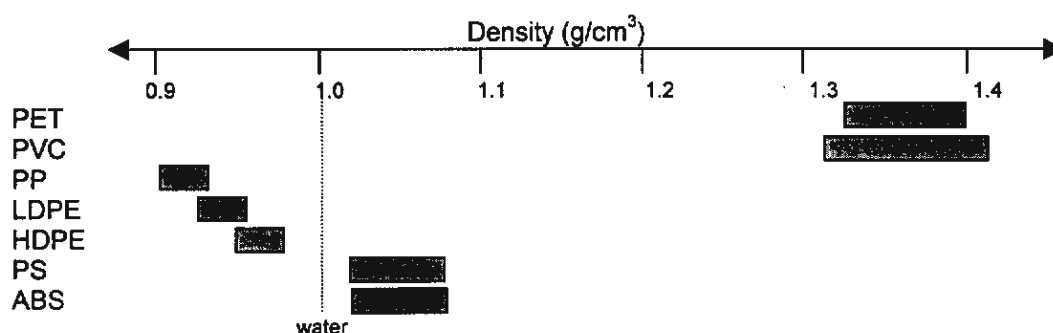


Figure 2.3 Density of common plastics

2.4 Recycling trend in Thailand (rewritten from International Forum of the Collaboration Projects, 2001)

Thai government's recycling effort is only at a planning stage. Although the volume of waste increases rapidly, it is not enough a pressure for the government to commit in waste reduction due to lands abundant and lack of awareness. In the private sector, small-scale waste buyers, scavengers, and collection crew practice recycling for revenue-earning purpose. A few local communities and private companies have initiated recycling programs recently but only as small pilot projects. Based on other and the project's surveys, it was estimated that the proportions of potential recyclable waste and potential commercial recyclable materials in the country total waste stream were about 45% and 35% respectively. However, actual recycling rates for urban areas by collection crew and scavenger was about 5%, and 10-15% if the amount sorted by households and sold to small waste buyers were included. Current recycling rates for glass, paper, plastics, and metal are about 10-40%. The market value of the recyclable materials is about 15,000 million bath per year, excluding various economic benefits such as environmental values and employment. The recyclable material market in Thailand is inefficient due to low quality and quantity of the collected recyclable materials. As a consequence, manufacturing recyclable material has to operate in a small scale, mostly as a family- type business. In general, low-quality recycled products are produced. There are also a few commercial-scale and capital-intensive manufacturers that use recyclable materials in their production. However, it has developed on the basis of imported recyclable materials and motivated by cost reduction in raw materials. Current recycling situation in Thailand suggests that Thai individuals as well as government and enterprises must have a greater awareness and motivation to participate in recycling.

2.5 Selective flotation

Flotation was originally patented in 1906 and has allowed the effective and efficient separation of low-grade and complex minerals and ores that were once unrecoverable. Hence, flotation is undoubtedly the most important and versatile mineral-processing technique. This application is being expanded to treat greater and to cover new areas. In the 1970s, the Mitsui Mining & Smelting Company first developed a froth flotation method for separation mixed plastics. The process was shown to be able to separate PP from PE. But, there are few full-scale applications of this technique in industry at present. However, this subject is now being focused on more and more. This section provides a technological and principles of plastics flotation.

Flotation is a surface-chemistry based on different wettability at solid particle-surface of plastics. Material surfaces are often naturally wettable by water and termed

hydrophilic. A surface that is non-wettable is water repelling and termed hydrophobic. If a surface is hydrophobic, it is also typically air attraction, termed aerophilic and strongly attracted to an air interface, which readily displaces water at the plastics' surface. In flotation, separation of a binary solids mixture may be accomplished by the selective attachment of hydrophobic particles to gas bubbles (typically air) (Rubinstein, J.B., 1995). The other hydrophilic particles remain in the liquid. The difference in the density between air bubbles and water provides buoyancy that preferentially lifts the hydrophobic particles to the surface where they remain entrained in a froth which can be drained off or mechanically skimmed away, thus, effecting the separation.

2.6 Related works

As mentioned above, the application of flotation for the separation of plastics waste mixtures is relatively new. Flotation was originally developed for ore separation about a century ago.

Early studies on plastics flotation were concerned with testing depressants (wetting agent) used in ore flotation or with optimising the hydrodynamics of the flotation device used (Saitoh K., *et al.*, 1976, Valdez E.G., *et al.*, 1979, Vogt V., 1981). An earlier report describing the separation of plastics by gamma flotation was published by Yazar B., in 1982. Using MIBC as a frother and exploiting the inherent hydrophobicity of plastics labels, the process was shown to separate cellulose from bottle labels as well as record-sleeve lamination.

Some of the patents obtained on the separation of plastics aimed mainly at flotation separation of PVC from other plastics (Izumi, S., 1975, Sisson, E.A., 1992, Kobler, R.W., 1995) because burning of PVC during waste processing lead to generation of hydrogen chloride gas that is environmentally hazardous. More extensive works focusing on the fundamental research on plastics flotation was done by several authors recently.

Later studies also considered alternative surface treatment by utility specific chemical and physico-chemical properties of plastics, such as critical surface tension, chain degradation, absorption from solution, etc.

Jordan C.E., *et al.* (1992) reported the flotation separation of PET and PVC. The clean PET and PVC mixture was conditioned in a gelatine solution and floated in the short flotation cell. In a single flotation step, over 75% of PET were recovery as a high purity product containing 99.8%.

Buchan R. (1995) and Yazar B. (1996) presented a paper describing the application of gamma flotation to separating PVC and PET. In a 20%CH₃OH / 80% H₂O flotation medium containing MIBC at pH 11, PET recovery was 0% while, PVC recovery reached 92%.

Shibata *et al.* (1996) explored the flotation separation of four engineering plastics, namely PVC, polycarbonates (PC), Polyacetal (POM) and polyphenylene ether (PPE) by using common wetting agent. Sodium ligninsulfonate was found to be a good depressing for PVC, saponin/Aerosol OT combination was most effective in depressing PC.

Drelich *et al.* (1999) presented that 93 - 95% of PET could be separated from PVC by using strong alkaline solution in froth flotation process.

Ferrara, G. *et al.* (1999) used water with suspended cork particles, one may create a medium with a density as low as 0.75 g/cm³. Two or more materials with densities below 1 g/cm³ may be economically separated. PMP (0.83 g/cm³), the widely used commercial plastics could be separated from HPDE (0.95 g/cm³).

Guern *et al.* (2000) studied role of lignosulfonate salt to separate PET and PVC. Bivalent cations could help lignosulfonate salt to separate plastics better than alkaline cations.

Shen *et al.* (2002) separated plastics by using the wetting agent; methyl cellulose (MC). Polyoxymethylene (POM) and PVC were depressed at very low MC concentrations. On the other hands, ABS and PS have a high floatability.

These efforts resulted in a number of different techniques for the surface treatment of plastics particles to achieve selective bubble attachment in flotation.

Unfortunately, there is some mismatch between the current need of industry for flotation research and the actual academic work in this field. This is partly because in the majority of scientific research studies, samples of untreated virgin plastics are used and obtained results are seldom compared with results on actual industries samples (Fraunholz N., 2004). Thus, this research will deal with this problem. Instead of using virgin plastics, this study uses post-consumer plastics, the surface properties of which can be strongly altered in comparison with virgin resins of the same type. Furthermore, combination between sink-float separation and selective flotation technique will achieve more effective than only use flotation.

CHAPTER III

METHODOLOGY

This experiment consisted of 2 parts. Part one involved sink-float separation, the latter dealt with selective flotation technique. The experiment was done at least three times to ensure reproductivity of the data. Then average values of these data obtained from the replicated experiments were presented in this work.

3.1 Plastics samples

The samples of six different kinds of plastics wastes were

- Poly(ethylene terephthalate) – PET
- High-density polyethylene – HDPE
- Polyvinyl chloride – PVC
- Polypropylene – PP
- Polystyrene – PS
- Acrylonitrile butadiene styrene – ABS

The samples were post-consumer plastics and obtained from drinking bottles, milk bottles, pipes, yoghurt cups, drinking cups and cardboards respectively. The samples used for test consisted of a mixture of 3 g of each plastics type. Moreover they were different colour, which made it easier to analyse the concentrate samples through manual sorting at the end of each experiment. Each of the plastics waste samples were shredded by using scissors and screened. The sieve size fractions used in this experiment are 0.3 – 0.5 cm, the general size that recyclers used as shown in **Figure 3.1**.

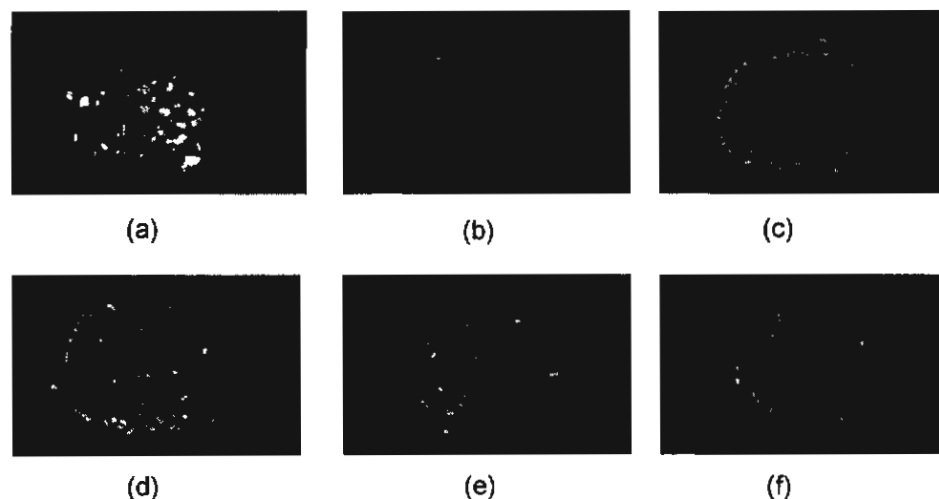


Figure 3.1 Schematic a configuration of each plastics
(a) PET, (b) HDPE, (c) PVC, (e) PP, (d) PS and (f) ABS