# 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 l ess d emanding p erformance r equirement; h ence the terms b ulk p lastics, 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 $^{\circ}$C or below 0 $^{\circ}$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 3 1 – 6 3 %, d epending o n t he a pplication a rea ( FTI, 2 001). P ackaging a pplications 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 c omprehensive i ntroduction o f c ommon p lastics 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)**.
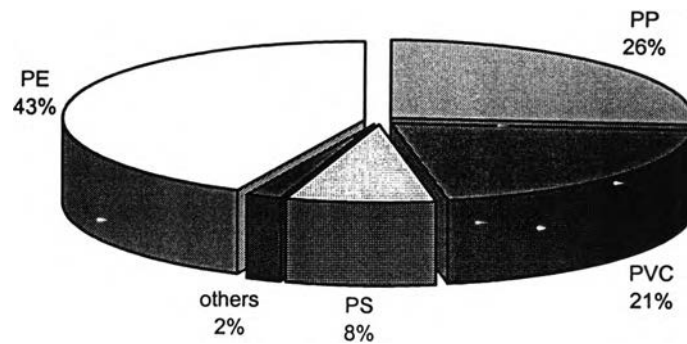
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[a] Polyolefins are PE and PP.

**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, T hailand i s t he f roth t hat d emands t wo m illion t ones f or plastics.

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

| Country | Population (millions) | GDP (Billions $US) | Demand for Plastics (million tones) | Employed by Industry |
|---|---|---|---|---|
| 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.

### 2.2.1 Polyethylenes (PE)

PE is the dominant thermoplastics material consumed in the world (Ehrig, R.J. *et al.*, 1992); include several copolymer of ethylene in addition to the homopolymer. The polyethylene homopolymer has the simplest chemical structure of any polymer **(Figure 2.2)**. In case of PE, a terminology has been adopted to classify materials in this family according to their densities, as shown in **Table 2.2**.

**Table 2.2** Density and acronym of polyethylene

| Polyethylene class | Density Range (g/cm³) | Acronym |
|---|---|---|
| Low density | 0.910 – 0.925 | LDPE |
| Medium density | 0.926 – 0.940 | MDPE |
| High density | ≥ 0.941 | HDPE |

PEs are partially crystalline materials. The amount of crystallinity depends on the branching of the polymer chains and determines the density of the material.

Materials produced by the high-pressure process fall primarily in the LDPE and the lower density end of MDPE classifications. These materials are generally termed "high-pressure, low-density polyethylene". Film for packaging is the largest single outlet for LDPE. Materials p roduced b y t he l ow-pressure p rocess s pan a ll three of the above classifications and are generally termed "linear polyethylene". The HDPE homopolymers are used for bottle and container applications.
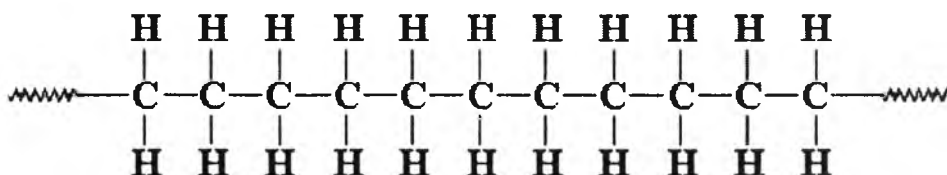


**Figure 2.2** Chemical structure of polyethylene

HDPE has the simplest structure and is essentially made of long virtually unbranched chains of polymer. These chains are able to align and pack easily; HDPE therefore has the highest degree of crystallinity in a polyethylene. Its molecular weight is high enough to obtain a degree of crystallinity as high as 70 – 95%. LDPE on the other hand has extensive chain branching in its structure and a cyrstallinity of only 40 – 60%. The amount of crystallinity and the melting temperature of the resin can even be further reduced by incorporating a small amount of a suitable co-monomer.

Recent market studies indicate very good prospects for polyolefins in general in the n ear t erm. L DPE is p resently growing at the f astest r ate while H DPE is c ontinuing t o compete e ffectively with v inyl i n p ipe m arket (Chemistry i n Britain, 2 001). I t i s a lso u sed extensively in bottles, containers, drums and house ware applications where its high modulus and very low permeability is particularly desirable. The high-density variety has the highest stiffness among polyethylene but moulded parts and thick films are opaque compared to the translucent LDPE products. The latter grade therefore finds a considerable market in films for packaging and agricultural use as mulch films, greenhouse films and irrigation pipes.

Blow-moulded products account for over 40% of the HDPE consumption with the milk and juice jugs being the primary packaging product. Only about 30% of the resin is used in injection-moulded products such as food containers and crates, while film applications account for about 7% of the HDPE consumption (Beach D.L., *et al.*, 1988)

### 2.2.2 Polypropylene (PP)

Since the mid 1950s when Ziegler-Natta catalysts that yielded high-molecular weight resin were discovered, the demand for polypropylene has increased dramatically. PP is a linear polymers (**Figure 2.3**) that typical manufactured by direct polymerisation of propylene in a low-pressure process by Ziegler-Natta polymerisations. PP of commerce are either isotactic homopolymer of propylene (this means that all the methyl groups are on the same side of the chain, **Figure 2.4**), random copolymers with mainly ethylene or butene-1 or multiphase block copolymers polypropylene-*block*-poly(ethylene-*co*-propylene). The polymerisation generally yields an isotactic index (generally measured as the percent insoluble in heptane) of 85 – 99. The isotactic form the polymer with a high degree of crystallinity (40 – 60%) is preferred for most practical applications. Isotactic propylene (iPP), the principal type used by the polymer processing industry, has a density about 0.92 – 0.94 g/cm$^3$. The atactic (means that the methyl groups are placed randomly on both sides of the chain form) is mostly amorphous and has a density only about 0.85 – 0.90 g/cm$^3$.
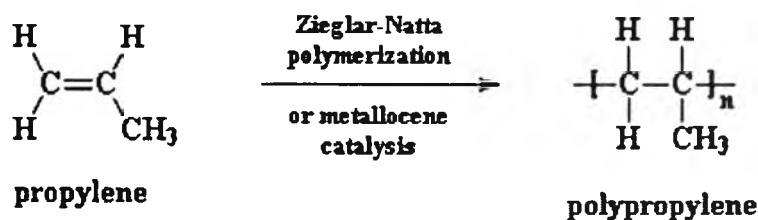
**Figure 2.3** Zieglar-Natta polymerisation of polypropylene

As the demand for polypropylene continues to create a large supply of low-cost resin **(Table 1.1)** and has excellent chemical resistance, there are potential for the resin to be used in applications presently using other types of commodity thermoplastics. Its replacement of polyethylene, however, is unlikely expected in applications that require high-temperature resistance where the use of iPP and its copolymer might be advantageous. The relatively poor weathering resistant of iPP limits its use outdoors. The majority market of PP is injection-moulded into products or spun into fibre for use in various textile applications. The latter includes sacks made of woven PP strips cut from oriented sheets used for packaging agricultural products. The common moulded products include closures, food containers, bottles, jars and crates. A relative small fraction of PP is extruded into film.
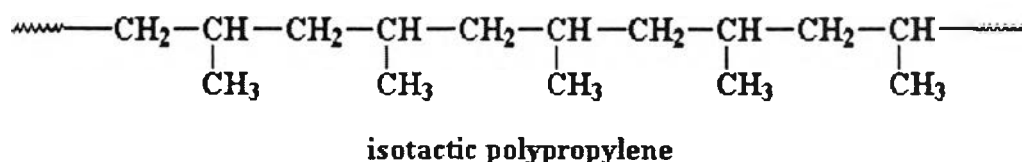


isotactic polypropylene

**Figure 2.4** Isotactic polypropylene structure

### 2.2.3 Poly(vinyl chloride) (PVC)

Poly(vinyl chloride), the second widely used resin in the world (after PE) is made by the polymerisation of vinyl chloride monomer (VCM). Vinyl is the industry term for thermoplastics containing vinyl chloride units $-CH_2-CHCl-$, although the vinyl of the chemical literature refers to any chemical compound with the group $CH_2=CH-$ (IUPAC: ethenyl). In theory the chemical structure of the polymer is simple, consisting of the same structure as polyethylene with one hydrogen atom in every other $-CH_2-$ group being replaced by a chloride atom. It is produced by the free radical polymerisation of vinyl chloride. However, as the repeat unit is asymmetrical because of the presence of only a single chloride atom, two types of linkage, head to tail and head to head are possible (Figure 2.5). In general, however, head to tail linkages are predominant (nearly 90%) in the resin. The crystallinity in PVC is due to syndiotactic sequence in the polymer and amount to about 7 – 20% in commercial resins. Resins with higher levels of crystallinity can be obtained by polymerisation under specific condition.
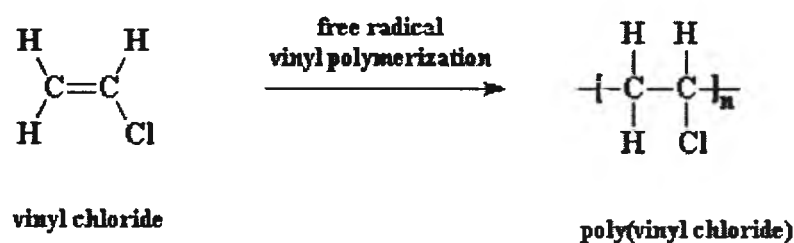


**Figure 2.5** Polymerisation of poly(vinyl chloride)

PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance it is used to make raincoats and shower curtains, and of course, water pipes. It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion. PVC resin can also be made into versatile soft pliable rubbery material by incorporating plasticizers such as organic phthalates into the compound. The diverse slate of PVC products can be broadly divided into rigid and flexible materials. Rigid applications, accounting for 60 percent of total vinyl production, are concentrated in construction markets, which include pipe and fittings, siding, carpet backing and windows. Bottles and packaging sheet are also major rigid markets. Flexible vinyl is used in wire and cable insulation, film and sheet, floor coverings, synthetic-leather products, coatings, blood bags, medical tubing and many more applications.

### 2.2.4 Polystyrene (PS)

General, polystyrene (also called crystal polystyrene because of the clarity of resin granules) is inexpensive, clear, hard, glassy material with a bulk density of 1.05 g/cm$^3$ and probably only polyethylene is more common in your everyday life. These desirable physical characteristics, as well as easy mouldability, low water absorbency and good colour range in which resin was available, made it a popular general-purpose resin. Its brittleness, which limited the range of products in which the resin could be used, was soon overcome when the high impact toughened grades of PS containing rubber became available.

Polystyrene is a vinyl polymer. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Polystyrene is produced by free radical vinyl polymerisation, from the monomer styrene (**Figure 2.6**).
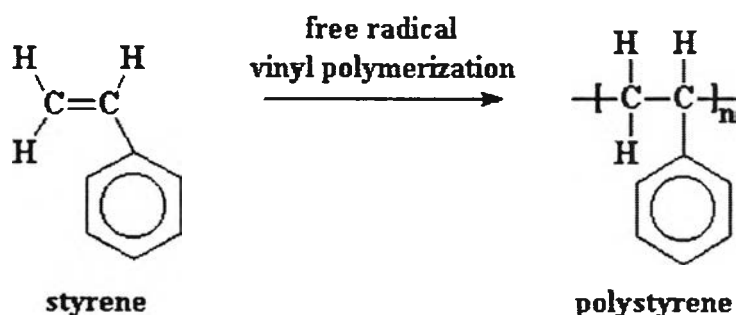


**Figure 2.6** Polymerisation of polystyrene

The resin is available as a general-purpose grade, high-impact resin, high-molecular weight resin (for improved strength), high-heat grades with a higher softening point and easy flow grades for sophisticated moulding applications. Impact grade resin accounts for about half demand for PS and is widely used in injection moulding of consumer products. Some copolymer such as acrylonitrile-butadiene-styrene copolymers (ABS), styrene-acrylonitrile copolymers (SAN) and styrene-maleic anhydride copolymers (SMA) are also commercially available. Copolymer of styrene with butadiene is an important elastomer widely used in passenger tire applications. PS foams are low-density packaging materials that provide exceptional insulation and bio-inert contaminant cost effectively. PS is popular used in hot beverage cups and food container, particularly in the fast-food industry.

## 2.2.5 Polyethylene terephthalate (PET)

PET has been known for many years simply as polyester **(Figure 2.7)** and was only known as fibre because the ester groups in the polyester chains are polar, with the carbonyl oxygen atom having a somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The positive and negative charges of different ester groups are attracted to each other. This allows the ester groups of nearby chains to line up with each other in crystal form. PET is a consideration polymer derived from terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG). Polymerisation occurs by heating these systems, typically with an antimony catalyst and removing either water or methanol. The condensation reaction occurs two steps. First, a low molecular weight precursor is formed, which is then transesterfied to form a high molecular weight reactor grade resin.

Generally, PET is clear, tough and has good gas and moisture barrier properties. The majority of PET ends up in soft drink bottles and blow moulded containers, although sheet applications are increasing. In addition, a small volume of PET is now used outside the packaging industry for the production of injection-moulded components such as bicycle mudguards. Cleaned, recycled PET flakes and pellets are in great demand for spinning fibre for carpet yarns and producing fibrefill and geotextiles. Other outlets include strapping, moulding compounds and both non-food containers and food containers (e.g., in boil-in-bag foods) as thermoformed sheets in frozen meal trays that can be heated in a microwave or even a conventional oven. Because of its good insulating properties, PET films are used in electrical device as well.

The best-known product made from aromatic polyester, however, is the blow moulded soda bottle, where the growth has been particularly dramatic during the past few years (Sustic A., 1991). This application accounts for 70 – 80% of the resin consumption and exploits the excellent barrier properties of the resin to carbon dioxide.
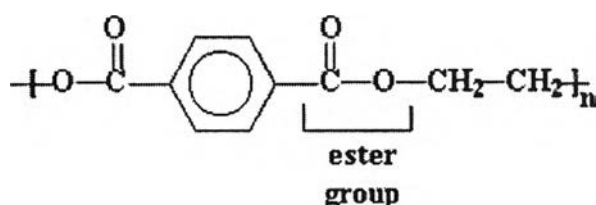


**Figure 2.7** Chemical structure of PET

## 2.3 Plastics wastes and plastics wastes management

At the end of the 1 9th century t he i ndustrial r evolution s aw t he r ise o f t he w orld o f 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 2.8**). 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.
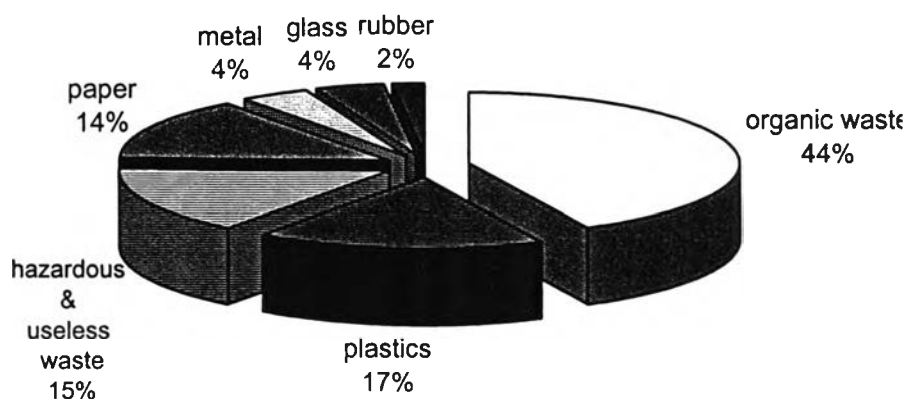


**Figure 2.8** Percent by weight of solid wastes in MSW, Bangkok 2000 (PCD, 2004)

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 stream 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 2.3**. 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 2.3** [a]SPI's voluntary plastics container coding system

| Plastics Identification Code | Name of plastic | Description | Some uses for virgin plastic | Some uses for plastic made from recycled waste plastic |
|---|---|---|---|---|
| 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. |
| | 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. | | |

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

- *Density-based sorting methods* predicated on density include sink-float tanks and hydrocyclones. Such techniques have been used widely for many years now and were the only technologies available for sorting waste plastics flake in early year of recycling. A major limitation of this method is that many plastics have virtually equivalent or fairly similar densities **(Figure 2.9)**. For instance, the density ranges of PE and PP can overlap and consequently these polymers cannot be separated by hydrocycloning. Likewise, both sink-float and hydrocyclone separation processes are unable to separate PVC from PET because the specific gravities of these two polymers overlap. Furthermore, these methods are limited use in case of plastics, which contain fillers, pigments and reinforcing agents, since these additives modify the density of the plastics.

> ➢ *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. 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.

- *Electrostatic sorting techniques* are generally based on the fact that whenever two dissimilar materials are brought into contact there is an exchange of charge across the interface, with one becoming negative and other positive. If one or both of these materials is an insulator, this acquire charge will be carried away when they separate. Usually there will be some relative movement between the two surfaces and this mechanism is consequently known as trobocharging.

- *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.
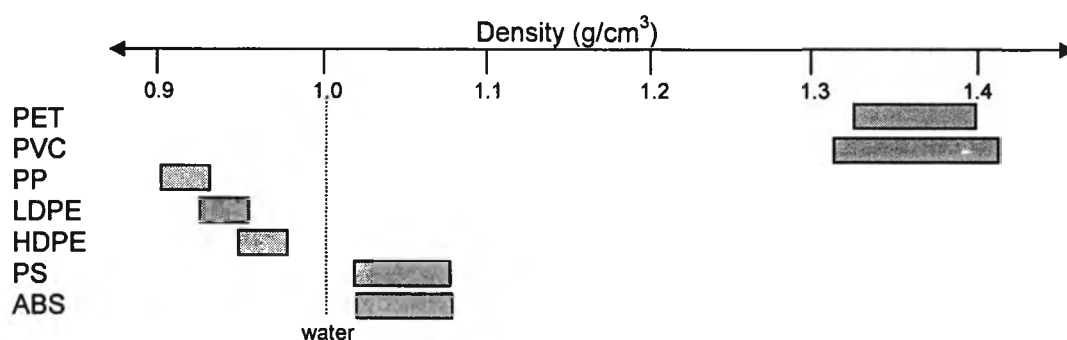


**Figure 2.9** Density of common plastics

**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 c ommercial-scale a nd c apital-intensive m anufacturers t hat 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.

### 2.5.1 The principle 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 aerophillic 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 b y t he s elective a ttachment o f 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 t hey r emain e ntrained i n a f roth which can be drained off or mechanically skimmed away, thus, effecting the separation.

### 2.5.1.1 Wettability

Flotation involves three phases (solid, liquid and gas) and corresponding potential phase interfaces into solid-liquid, liquid-gas, solid-gas and solid-liquid-gas. The hydrophobic or hydrophilic nature of the solids at the solid-liquid-gas interfacial region is determined by the wettability of the solid. A parameter that characterizes wettability is "the contact angle ($\theta$)" at the three-phases interface. The liquid is seemed wetting when $90 < \theta < 180$ degrees and non-wetting when $0 < \theta < 90$. $\theta = 0$, 180 degrees corresponds to perfect wetting and the drop spreads forming a film on the surface **(Figure 2.10)**.
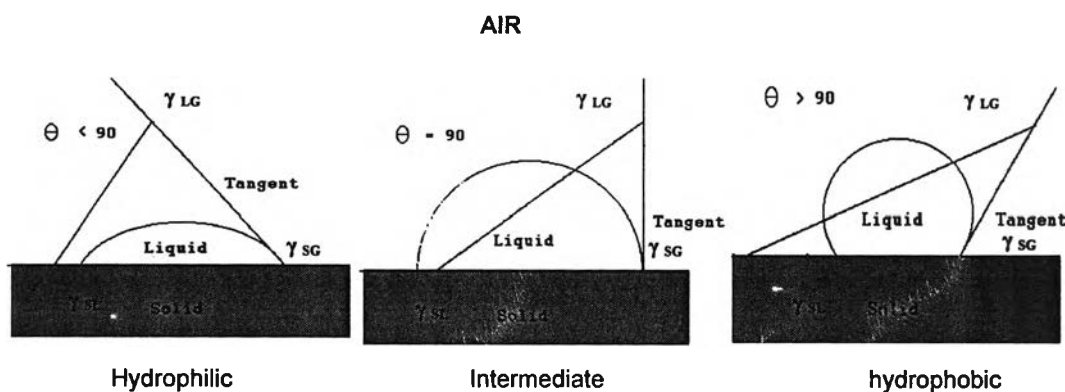


**Figure 2.10** Relative equilibrium states for a water droplet at a solid surface indicating various wettability regimes (adapted from www.ksvinc.com)

It can be seen from this Figure that low values of $\theta$ indicate the liquid spreads, or wets well, while high values indicate poor wetting. If the angle $\theta$ is less than 90 the liquid is said to wet the solid: hydrophilic. If it is greater than 90 it is said to be non-wetting: hydrophobic. A 90 contact angle may exist where the solid does not exhibit either strong hydrophilic or hydrophobic character. The contact angle is related to the respective interfacial surface tension ($\gamma_{SG}$, $\gamma_{SL}$ and $\gamma_{LG}$) by Yong's equilibrium equation.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta \qquad (2.1)$$

Generally, plastics are hydrophobic by nature (Gisela, A.M., *et al.*, 1999) and exhibit differences in surface energy as shown in **Table 2.5**. In case of the common plastics, PE is the highest hydrophobicity. Thus, in order to a successful separation using flotation, it is usually necessary to selectively enhance the hydrophobicity of one of the plastics components that is otherwise hydrophilic or not strongly hydrophobic. This selective modification of the wettability of plastics in froth flotation is obtained using additional reagent termed "wetting agent".

**Table 2.5** Surface tension ($\gamma_{SG}$) and contact angle of some plastics with water (Fraunholez, N., 1997)

| Plastics | $\gamma_{SG}$ (mN/m) | Contact angle (deg) |
|---|---|---|
| GRPP | 32.7 | 96.3 |
| PS | 43.0, 39.3 [a] | 86.3 |
| ABS | 42.7 | 83.7 |
| PC | 44.5 | 80.3 |
| PA6 | 43.8 | 61.4 |
| PMMA | 43.8 | 72.9 |
| PVC | 42.3, 41.9 [a] | 84.6 |
| POM | 44.9 | 71.2 |
| PET | 44.6 [a] | 76.5 [b] |
| PP | 29 – 31 [c] | 95.0 [b] |
| PE | 30 – 31 [c] | 96.8 [b] |

[a] from Shen H., et al., 2002

[b] from Dodbiba N., et al., 2002

[c] from www.accudynetest.com/surface_energy_materials.html

### 2.5.1.2 Wetting agents

To invoke selective hydrophobicity, substances known as wetting agents are used. Wetting agents are typically hetero-polar organic substances – they contain both non-polar and polar chemical groups. The non-polar end is almost always a long chain or cyclic hydrocarbon group that is hydrophobic. The wetting agent must be able to attach to the solid and it does so through its polar end, which is typically an ionic group termed the solidophil group.

When the solidophil group of a suitable wetting agent contacts a plastics surface site that can chemically interact with the solidophil group, the wetting agent bonds to the surface of the plastics via chemisorption, physisorption or ionic bonding. The non-polar end of the wetting agent then orients outward from the solid phase forming a non-polar chemical envelope surrounding the plastics particle, including hydrophobic behaviour on an otherwise hydrophilic plastics surface. The plastics particle can then more readily attach to an air bubble **(Figure 2.11)** via the hydrophobic end of the wetting agent.
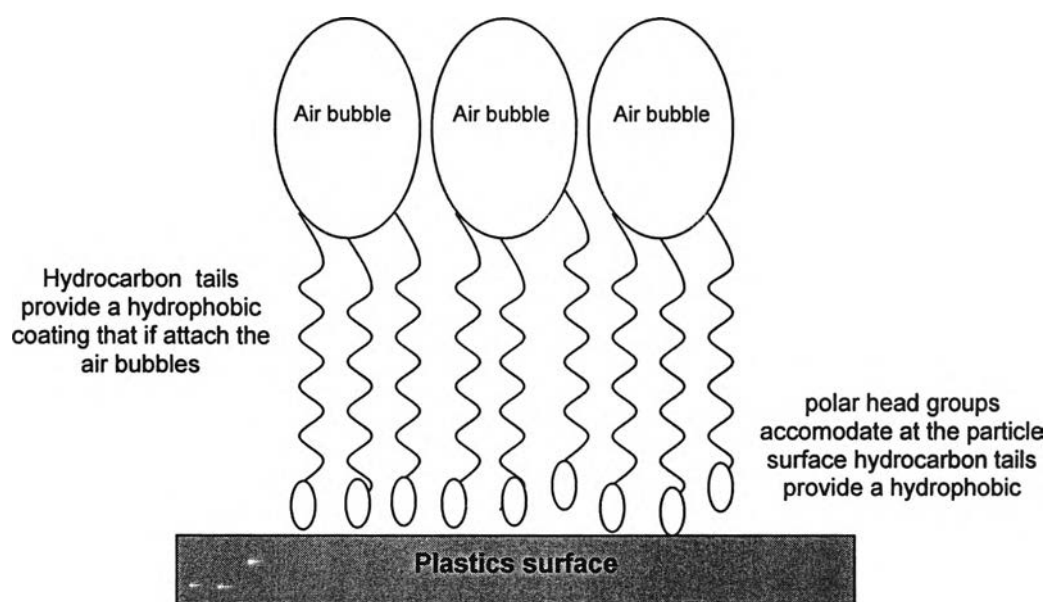


**Figure 2.11** Wetting agent alignment at plastics surface

Consequently, a key to successful flotation is to selectively induce, using a suitable wetting agent, hydrophobicity on the desire material to be recovered, while retaining hydrophilicity of the non-desirable material. It should also be noted that strength of the induced hydrophobicity of the plastics via the wetting agent is directly relatable to the length of hydrocarbon group, while the strength and selectivity of the wetting agent's ionic bonding is controlled by type of solidophil group.

There are many different types of wetting agents and they are classified from type of ion (anionic or cationic) that is formed upon their dissociation in aqueous solutions. For example, calcium lignosulfonate (CaLS) is a widely used as a wetting agent for minerals separation **(Figure 2.12)**. It is comprised of a long chain non-polar hydrocarbon group, lignin, which is hydrophobic and a polar sulfonate group. Lignosulfonate is a by-product of the paper industry and low toxicity. A study performed in a Hallimond cell has led us to select a lignosulfonate that renders PET hydrophilic (LeGuern C., *et al.*, 1997). Although, the depressant action of lignosulfonate on plastics has been known since 1970s (Saitoh K., *et al.*, 1975).

Lignosulfonate is an anionic polymer in which the essentially hydrophobic backbone is rendered hydrophilic by sulfonate group's substitution. The molecule is highly crosslinked and also contains some carbonyl groups. If pH is more than 9, the phenolic hydroxyls in the molecules dissociate and the negative charge of the molecule increase strongly (Hachey J.M., *et al.*, 1992). In aqueous solution, the lignosulfonate assumes a roughly spherical shape. Lignosulfonate is also noteworthy for its polydispersity with regard to molecular weight and structure as well as distribution of the monomer units. However, in order to make selective flotation completed, there is another chemical, which helps solidophil attach the air bubble strongly and float to the top of the flotation column stably. It is a "frother".
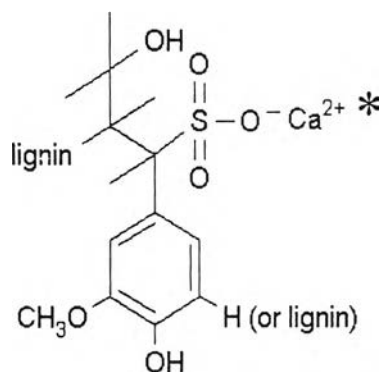


Figure 2.12 Chemical structure of calcium lignosulfonate

### 2.5.1.3 Frothers

In addition to wetting agents, another important component in successful flotation is the presence of frothers. Once its surface is rendered hydrophobic, a plastics particle must be able to attach to an air bubble. While it may be possible to initially obtain plastics particle attachment to air bubbles in an agitated liquid under aeration alone, these air bubbles are unstable and quickly break down due to collisions with other air bubbles, plastics particles and the vessel wall. Furthermore, the bubble size may not be sufficient to effectively carry a plastics particle to the surface of the liquid. Consequently, additional reagents, termed frothers, are added to promote the formation of stable air bubbles under aeration.

Frothers, like wetting agents, are typically comprised of both a polar and non-polar end. The non-polar hydrophobic ends orient themselves into air phase. Bubble wall strength is enhanced by simultaneous strong polar-group and water-dipole reaction at the air-liquid interface resulting in greater bubble stability due to a localised increase in surface tension.

Frothers are generally classified by their polar group with the most common being the hydroxyl (–OH), carboxyl (–COOH), carbonyl (=C=O), amino (–NH$_3$) and sulfo (OSO$_2$OH and –SO$_2$OH) groups. Table 2.6 lists some common frothers according to their chemical grouping. Effective frothers typically contain at least five or six carbon atoms in their strength chain, non-polar group to obtain sufficient end and stable interaction with the air phase. For branch-chain hydrocarbons, the number of carbon atoms in the polar group may range up to sixteen. However, a frother must be at least slightly soluble in the liquid medium and increasing the straight-chain hydrocarbon length will eventually lead to too low of a solubility for effective frothing. Thus, a suitable frother must provide a balance between sufficient non-polar interaction with air and solubility in water. With respect to the polar groups, one or two are usually sufficient to interact at the liquid-air interface to provide sufficient frothing properties and additional polar groups provide benefit.

Most of the frothers in Table 2.6 are hydroxyl-group-type frothers and have little wetting agent properties. However, because of the inherent hetero-polarity of wetting agents, a wetting agent can also serve as a frother in some system. This is true of carboxyl-type frother, sodium oleate and sulfo-solidophil fatty acid.

Certainly, wetting agent/frother combination may also exhibit a synergistic separation effect. However, the designs a flotation system based upon a wetting agent specific to the modification of the surface properties of the plastics required for separation. The type of frothing agent is a secondary consideration that is chosen after the wetting agent to provide suitable frothing conditions and non-interface with wetting agent or separation system.

**Table 2.6** Examples of some common frothers (The Dow Chemical Company, 1986)

| Frother | Formula |
|---------|---------|
| Aliphatic alcohols | |
| • Methyl isobutyl carbinol (MIBC) | $CH_3CH(CH_3)CH_2(OH)CH_3$ |
| • Di-acetone alcohol | $(CH_3)_2(OH)CH_2COCH_3$ |
| • 2-ethyl-3-hexanol | $CH_3(CH_2)_3CH(C_2H_5)CH_2OH$ |
| Cyclic alcohols | |
| • Pine oil (terpineol) | $C_{10}H_{17}OH$ |
| • Eucalyptus oil (cineole) | $C_{10}H_{16}O$ |
| Phenols | |
| • Cresol | $CH_3C_6H_4OH$ |
| • Xylenol | $HOCH(CHOH)_3CH_2OH$ |
| Polyglycols | |
| • Poly(propylene glycol) monalkyl ether | $R(OC_3H_6)nOH$, $n = 2 - 5$, $R = CH_3$, $C_4H_9$ |
| • Poly(ethylene glycol)s | $R(OC_2H_4)nOC_2H_4OH$, $n = 2 - 5$ |
| Other | |
| • Sulfo-cetyl alcohol | $CH_3(CH_2)_{14}CH_2OsO_2OH$ |

## 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 Yarar 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 Yarar B. (1996) presented a paper describing the application of gamma flotation to separating PVC and PET. In a 20%$CH_3OH$ / 80% $H_2O$ 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/cm$^3$. Two or more materials with densities below 1 g/cm$^3$ may be economically separated. PMP (0.83 g/ cm$^3$), the widely used commercial plastics could be separated from HPDE (0.95 g/ cm$^3$).

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 (Fraunholcz 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.