CHAPTER II
LITERATURE SURVEY

2.1 High Density Polyethylene

High density polyethylene (HDPE) is a thermoplastic polyolefin manufactured by ethylene polymerization with density of 0.94 g/cm^3 or higher, depending on the thermo-mechanical histories of the samples. HDPE was first prepared from diazomethane in the early 1950's, either by the Phillips or Ziegler-Natta process.

2.2 Recycling of HDPE

The technology of recycling can be directed at four modes of sources which are use as generic plastic, use of mixed plastic, regeneration of raw materials, and use in energy recovery (Cornell, 1995).

Polyethylene can be recycled by many modes of technology. The first one is primary recycling which transforms a product into a product similar or identical to the original. Next is use as generic plastic, which is called the secondary recycling. The method of this technology is processing of waste into a product which fewer requirements of physical and chemical properties. Moreover, polyethylene can be use in energy recovery or quaternary recycling because the recoverable energy contents of plastic that can be captured during combustion. (Cornell, 1995) However, each technology is not justified as the best to other due to the economic reasons should be considered in case by case.

HDPE bottle recycling is attractive because of several factors:

A. large quantities of HDPE scraps produced each year;

B. the bottles are usually blow-molded from HDPE;

C. HDPE is easy to reprocessed;

E. there exist technological know-how to recycle HDPE.

Applications of recycled HDPE bottles are large containers, blow mold bottles, bottle crates, drainage pipes, garbage bag etc.

2.3 Print Screen Ink

Ink is defined as a dispersion of pigments or dyes in a fluid carrier. The types of printing screen inks for commercial use in the plastic packaging industries are ultraviolet curing printing inks and conventional inks. UV curable inks, which compose of a photo initiator, are usually used for printing on plastics closures (e.g., caps, lids, etc.) while conventional inks are used in screening and pad printing of a rigid plastic container (e.g., a blow-molded bottle).

Conventional printing inks are composed of pigment carriers, resins and additives. Organic and inorganic pigments give colour and opacity to the ink and influences its fluidity. Resins, which are mostly low molecular weight polymeric resins, is responsible for dispersing and retaining the pigment on the plastic surface after printing. The carrier is a liquid that provides fluidity for the ink and transfers the ink from the printing system to the plastic substrate, and after application of the ink onto a surface, the carrier should evaporate quickly. Additives in the ink include waxes, surfactants, drying agents and anti-oxidizing agents.

Conventional printing inks are classified as either solvent-based or water-based, depending on the type of the carrier used. The carriers for solvent-based inks are solvents, solvent mixtures, or water miscible solvents. Water-based inks use water as the carrier, which could contain up to 20%

alcohol (Gecol, 1998). Besides, the resin used in water-based inks is usually called a binder.

Table 2.1 Print screen inks formula.

Ingredients	Part per hundred
for polyethylene bottles	
- organic pigment	5.0
- titanium dioxide	11.0
- long oil epoxy ester	82.0
- naphthenate catalysts	2.0

Source: Encyclopaedia of Polymer Science and Engineering, 2nd edition, Vol. 13,1996.

It is essential that the ink wets the surface of the plastic to produce a uniform covering and bond strongly to the surface during printing. Since it is generally known that polyethylene is an excellent chemical resistant, . the nature of polyethylene is largely resistant to chemical attack and a little effect by electrical fields (Peacock, 2000). Hence, there are a number of treatment processes applied for plastic surface in order to increase the surface energy of the plastic and thereby enhance the wetability of the ink. These treatment processes are chemical treatment, flame treatment, corona discharge treatment, plasma treatment, and ultraviolet treatment. Flame treatment is the most common process used to improve ink adhesion to mold polymer such as rigid plastic containers.

It is believed that flame treatment oxidizes the surface of the plastic and makes it more easily wettable. Flames contain exited species of O, NO OH, and NH, which can remove hydrogen from the substrate surface. The oxidation that follows is thought to propagate by a free radical mechanism.

The plastic surface is contacted for a period of less than 1 second with the oxidizing portion of the flame. The gas is burned using 10% - 15% excess air over the stoichiometric ratio in order to obtain an oxidizing flame with a temperature of 1090 - 2760^{o}C (Santuss, 1986).

2.4 Surfactant

2.4.1 The Nature of Surfactant

A surfactant or surface active agent is a substance that when presents at low concentration in a system, has the property of adsorbing onto the surface or interfaces of the system and altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces (Rosen, 1989). It is a polar compound consisting of an amphiphilic molecules, i.e. a molecule with a hydrophilic head attached to a long hydrophobic tail (Kouloheris, 1989). At a partial concentration (know as the critical micelle concentration, CMC) surfactant molecules become more favourable to form aggregates called micelle as shown in Figure 2.1. A surfactant can be replaced in one of four classes, depending on what charge is present in the chain-carrying portion o the molecule after dissociation in aqueous solutions (Jakobi and Lohrl,1987).

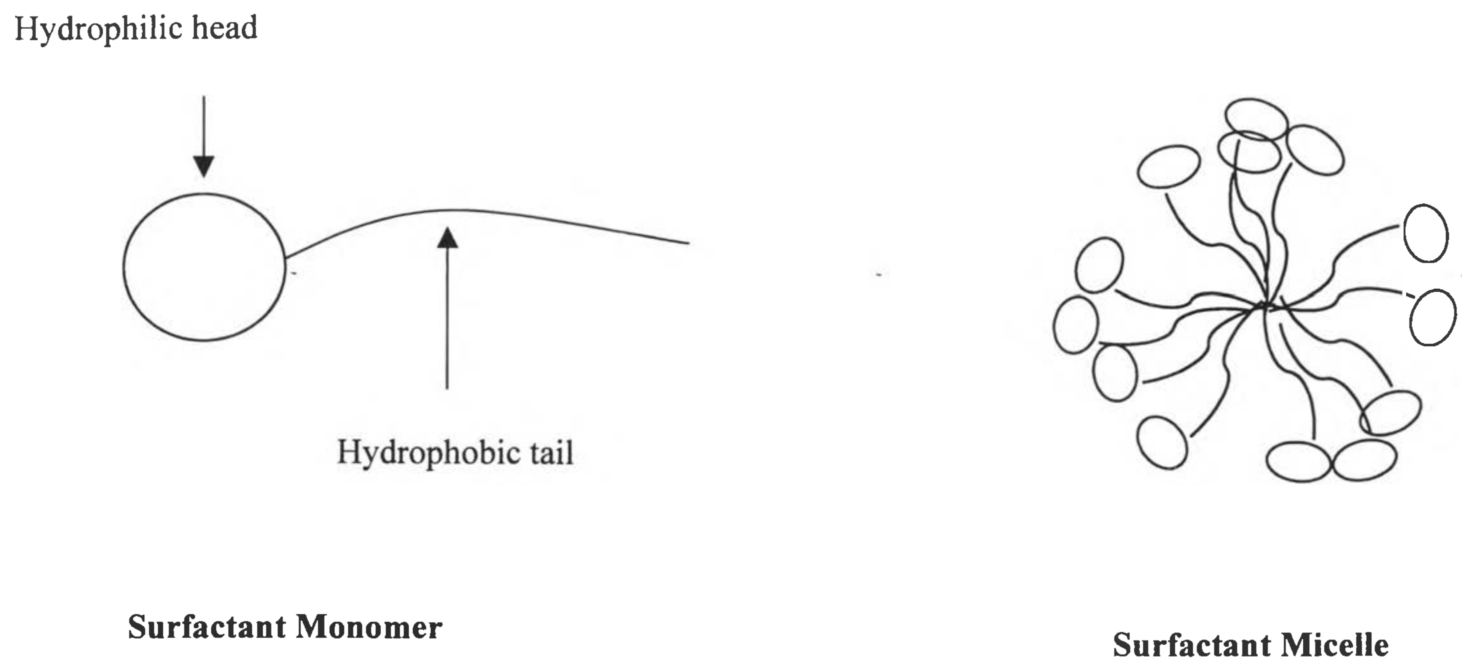

Figure 2.1 Surfactant molecule/ion, and a representation of a surfactant micelle in a surfactant solution some what above the critical micelle concentration (adapted from Wilson and Clarke, 1994).

2.4.2 Mechanism of Deinking

There is no clear mechanism that describes the removal of ink from HDPE surface by surfactant yet. However, there are two theories support the deinking mechanism which are:

2.4.2.1 Roll – Backed (Roll-Up) Mechanism

Removal of liquid (oily) soil by aqueous solutions is accomplished mainly by a roll-up or roll-back mechanism in which the contact angle that the liquid soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath (Rosen, 1989).

In the laundering process, the mechanism of soil removal from cloth fibre depends on whether the soil type is solid or liquid. Therefore, it seems reasonable to suppose that the mechanism of ink removal is dependent on the ink type. The shape of a liquid droplet or film can change during soil removal, permitting the surfactant to occupy the vacated space. Ink roll-back can occur wets the ink film on the polymer surface. As s result, the film rolls back to form droplet. Figure 2.2 is an illustration of how 100% ink removal occurs. In reality, however, some ink may be left behind. Such marginal roll-back has been proposed to occur in the laundering of liquid soils.

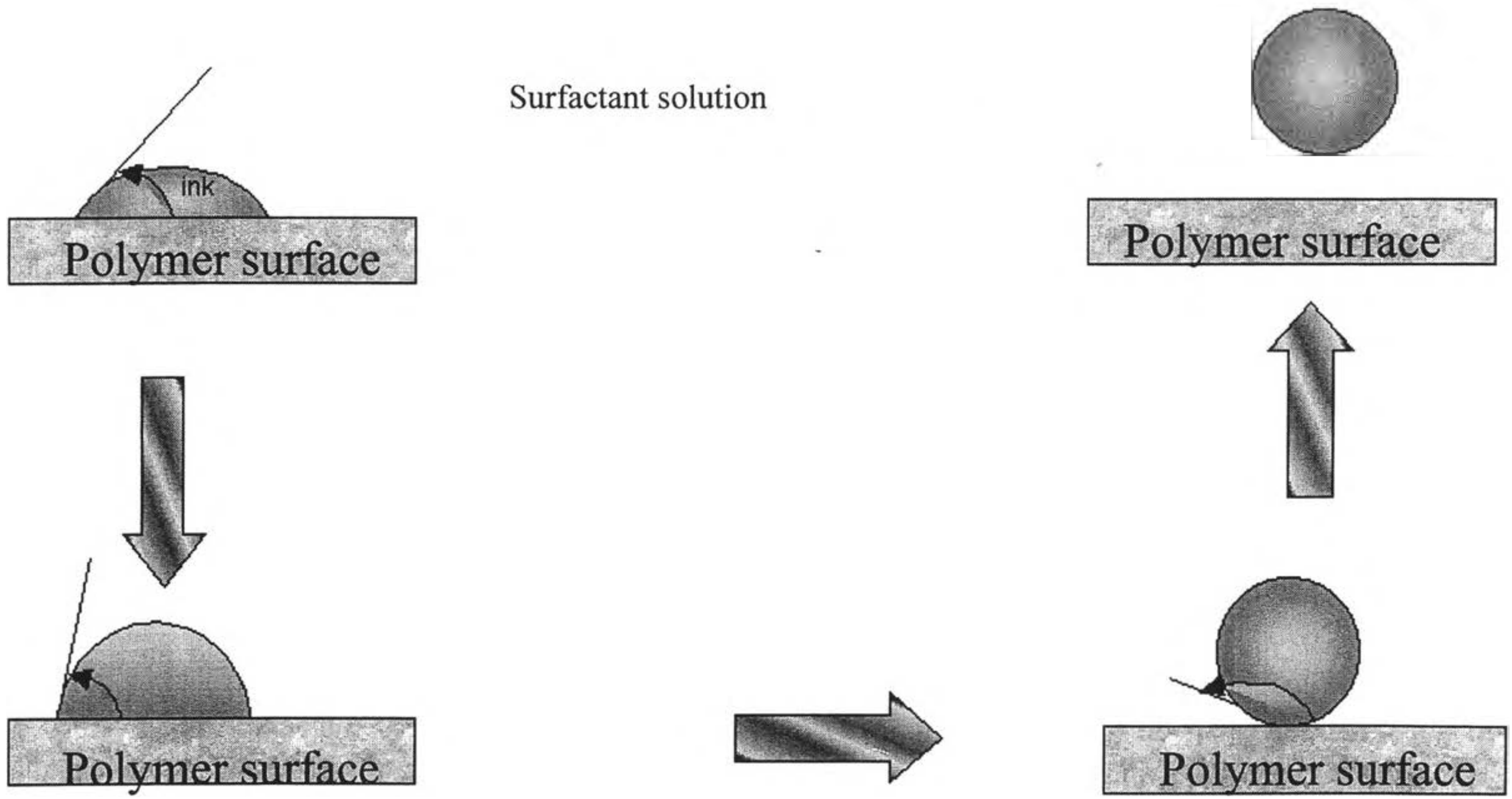

Figure 2.2 Detachment of ink from a polymer surface by the Roll-up mechanism (adpter from Borchardt, 1994).

2.4.2.2 Solubilization

If the deinking surfactant is above its CMC, ink solubilization can occur by the process illustrated in figure 2.3

Solubilization consists of the following steps:

A. Diffusion of surfactant micelles to the ink surface.

B. Adsorption of the micelle at the ink/water interface.

C. The ink species mix with the surfactant molecules.

D. The micelle desorbs from the surface with ink in the interior of the micelle.

E. The micelle diffuses into the bulk of the solution.

Step A and step C can be promoted by hydrodynamic flow of the aqueous phase during deinking, i.e. by agitation of the mixture.

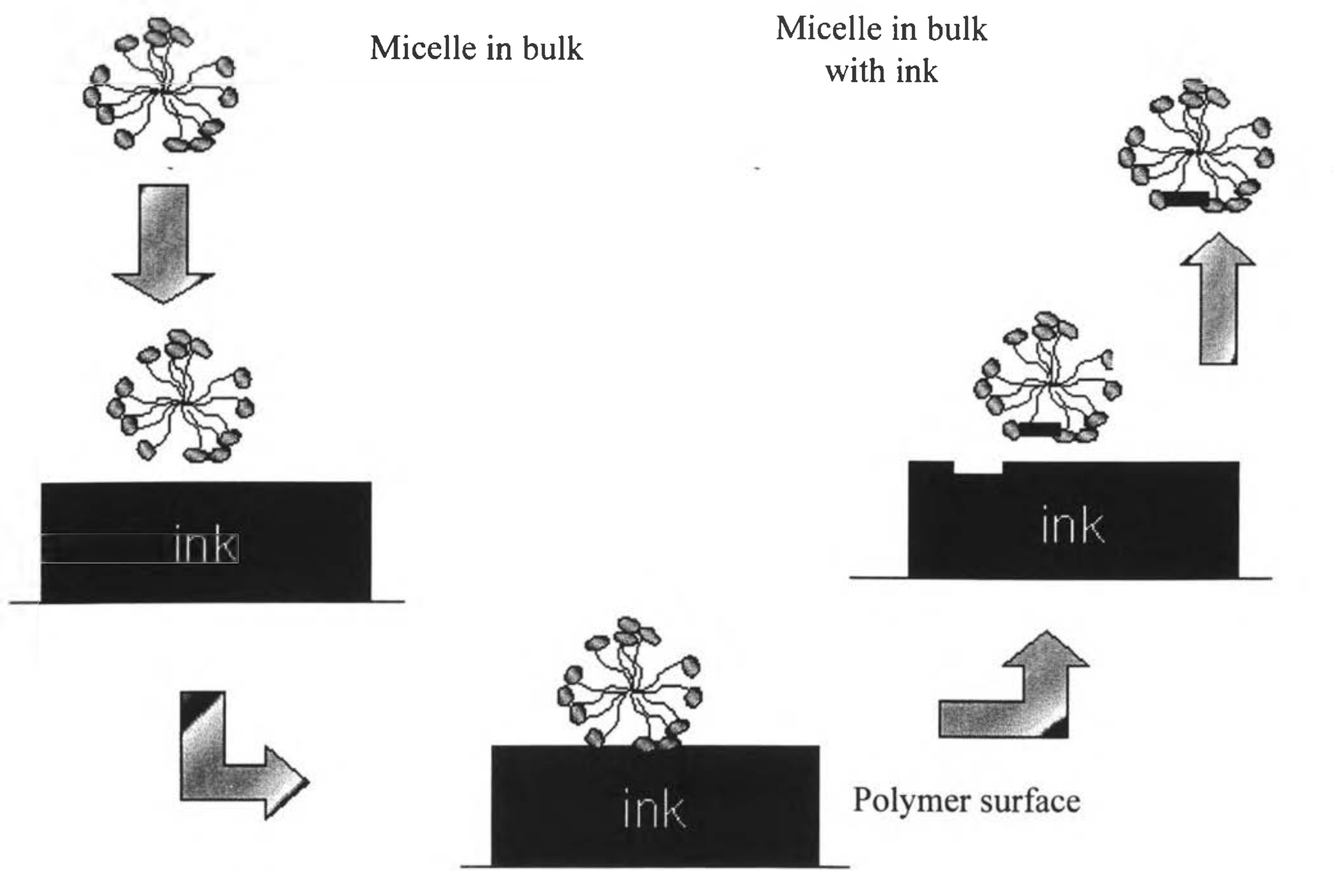

Figure 2.3 Detachment of Ink from a polymer Surface by the Solubilization mechanism (adapted from Borchardt,1994).

2.4 Related Work

Pattanakul *et al.* (1991) investigated the effect of virgin HDPE/ recycled HDPE from milk bottle composition on the mechanical and physical changes. They indicated that there was no change in the flow properties and no there was no effect of composition on tensile strength observed. In addition, they suggested that the recycled HDPE from milk bottles was a material with useful properties that did not show the significant different properties from those of the virgin material.

Doyan *et al.* (1994) observed the processability and the mechanical properties of closed-loop extruded HDPE. They showed that the molecular weight obtained from intrinsic and crystallinity is higher after 10 cycles than after 1 cycle. They also concluded that both chain scission and crosslinking occurred simultaneously during extrusion. Chain scission is the dominant factor for the first cycle and crosslinking take over after a while because of the accumulation of free radical during extrusion.

Arthasat *et al.* (1996) studied blends of virgin/post consumer HDPE from water bottle at different ratios ranging from 0% to 100% post-consumer HDPE after reprocessed for 10 passes using twin screw extruder. It was founded that virgin HDPE and blends of virgin/post-consumer HDPE can be reprocessed at 235 ^{O}C for 10 passes with better processability, decreasing in viscosity and percentage of crystallinity, small changing in mechanical properties. A decreased in MFI is hypothesized to be due to crossliking or chain branching rather than to chain scission.

Malloy *et al.* (1998) studied the effect of multiple recycle history on the mechanical properties of homopolymer bottle flakes and pigmented HDPE homopolymer flakes by selecting white HDPE bottle flakes. They found that both natural HDPE and white HDPE which are treated as separate material steam can be recycled as much as 12 cycles and also exhibit excellent property retention.

They also investigated the effect of white HDPE homopolymer bottle flakes on the properties of mixed color HDPE bottle flakes by blended white HDPE together with mixed color HDPE bottle flakes at variation % composition. The result showed that the mechanical properties of the mixed color HDPE is altered to a limited degree by the addition of the white HDPE homopolymer. The addition of white HDPE to the mixed color HDPE resulted in a somewhat stiffer, stronger, but less ductile formulation.

Gecol *et al.* (1998) studied the properties of re-extruded plastic film. They founded that plastic film contaminated with heavy printing is not suitable raw material for clean plastic film recycled production cause the decreasing and variation of physical properties, pellet cracking and color from residual ink. Ink contamination makes the plastic less stiff and weaker. The reason for this is agglomeration of ink particle which act as stress concentration point reduces the strength.

They also observed the usage of different of surfactant solutions for deinking of polyethylene plastic films printed with water-based ink by flexographic process at various pH levels. The results showed that the cationic surfactant is the most effective on deinking of water-based inks at all pH values studied. In addition, they also investigated on the solvent-based ink removal. They founded that the cationic surfactant is the most effective surfactant but requires a pH value of 11 or higher.

Min (1999) studied the effects of surfactant type, pH, surfactant concentration, and abrasive on the removal of solvent-based ink from HDPE containers. cationic, anionic , and non ionic surfactants were used under basic pH conditions. ATR-FTIR spectroscopy and optical scanning methods were used to determine the degree of deinking. Cationic surfactants at concentration above the CMC at pH 12 were the most effective system studied.

Songsiri (2000) investigated the effects of cationic surfactant concentration, pH level, process temperature, pre-soaking time, shaking time, and abrasive were investigated for solvent-based ink on HDPE surfaces. The results showed that the cationic surfactant was effective only at concentration above the CMC and at high pH levels. At both below and above the CMC, ink removal was promoted by increasing temperature, pre-soaking time, and shaking time. The presence of an abrasive also helps to detach the loosen ink from plastic surface.