CHAPTER IV

RESULTS AND DISCUSSION

4.1 Sink-Float method

The plastics mixture was first separated by using water as medium solution. From the result, it was possible to separate six plastics into two groups **(Figure 4.1)**. The first group (Group I) included PET, PVC, PS and ABS. They were depressed in water therefore, they sank in the bottom of the cell because the density of this group was higher than that of water. While, the second one (Group II) including HDPE and PP were floated to the surface of this medium. The densities of these plastics are shown in **Table 4.1**.

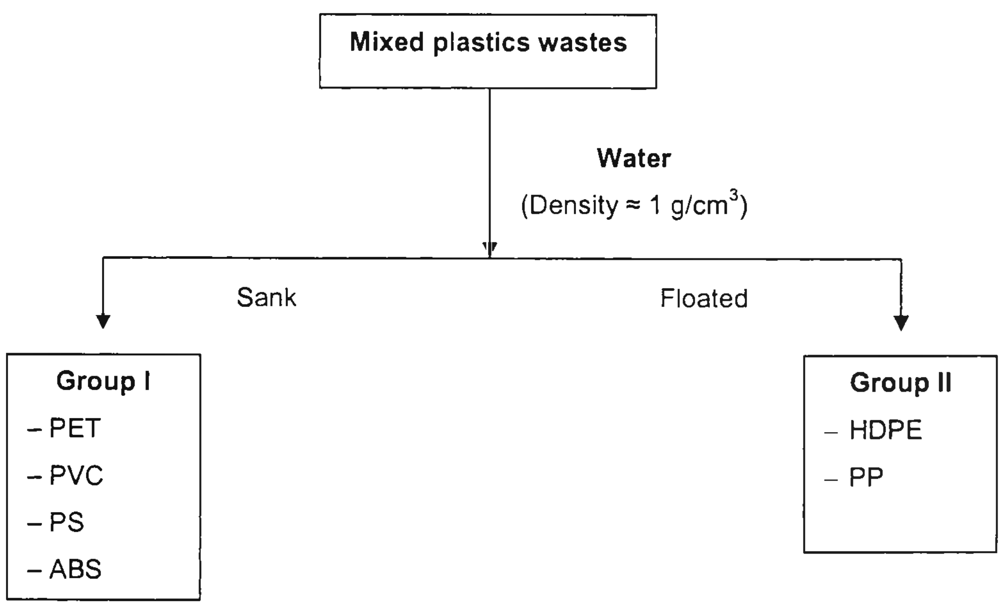

Figure 4.1 Plastics separation by using water

Each plastics in Group I and in Group II were individually separated by dense medium solution and light medium solution, respectively in the next step. In all these experiments, calcium chloride aqueous solution with various concentrations meant dense medium solution (DMS) and ethyl alcohol solution with various concentrations meant light medium solution (LMS).

4.1.1 Dense medium solution

To separate plastics in Group I individually, calcium chloride aqueous solution was then used as a dense medium solution (DMS) through all the experiments. The results showed that when applying DMS at 10 – 30 %w/v concentration, PET and PVC sank to the bottom of the solution whereas, PS and ABS floated to the surface of the solution. Then the plastics in Group I were separated into two sub-group: PET/PVC and ABS/PS as shown in Figure below.

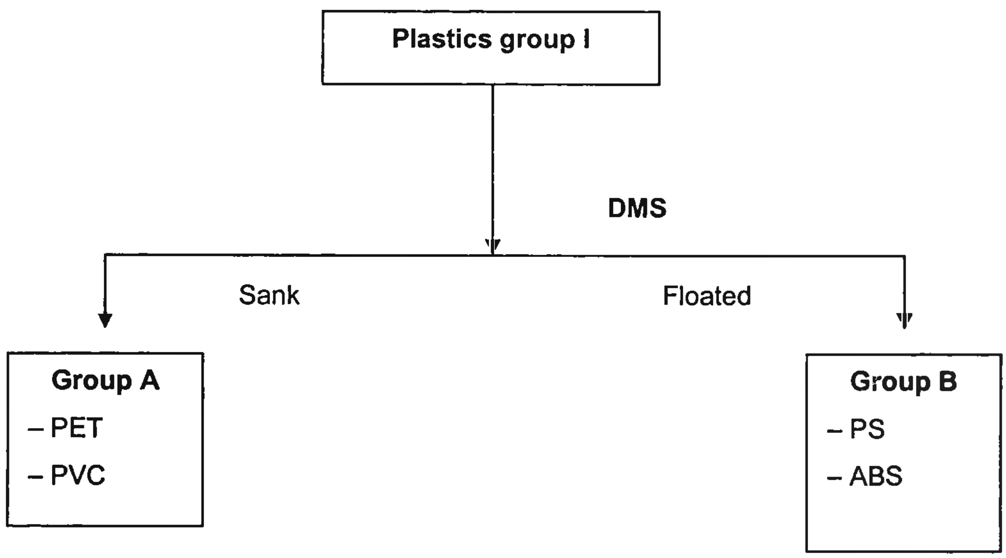

Figure 4.2 Plastics separation by using dense medium solution

When using DMS at high concentration (more than 30 %w/v), some PET and PVC thus floated to the solution surface. All PET and PVC floated to the surface when DMS concentration was 60 %w/v. The floatability [a] of these plastics is shown in **Figure 4.3**. From all above, it could be seen that PS and ABS were separated from PET and PVC by DMS at 20 %w/v. It was discovered that density of DMS varied with concentration of calcium chloride from this experiment as shown in **Table 4.2**.The densities of PET and PVC were higher than that of 10 – 30 %w/v DMS concentrations but the densities of PS and ABS did not.

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[a] Floatability calculation *sees* **Appendix B**

From the Figure below, although, at 30 %w/v of DMS the recovery of plastics was a little bit higher than 20 %w/v but taking the environmental and cost effective in consideration at 20 %w/v was better.

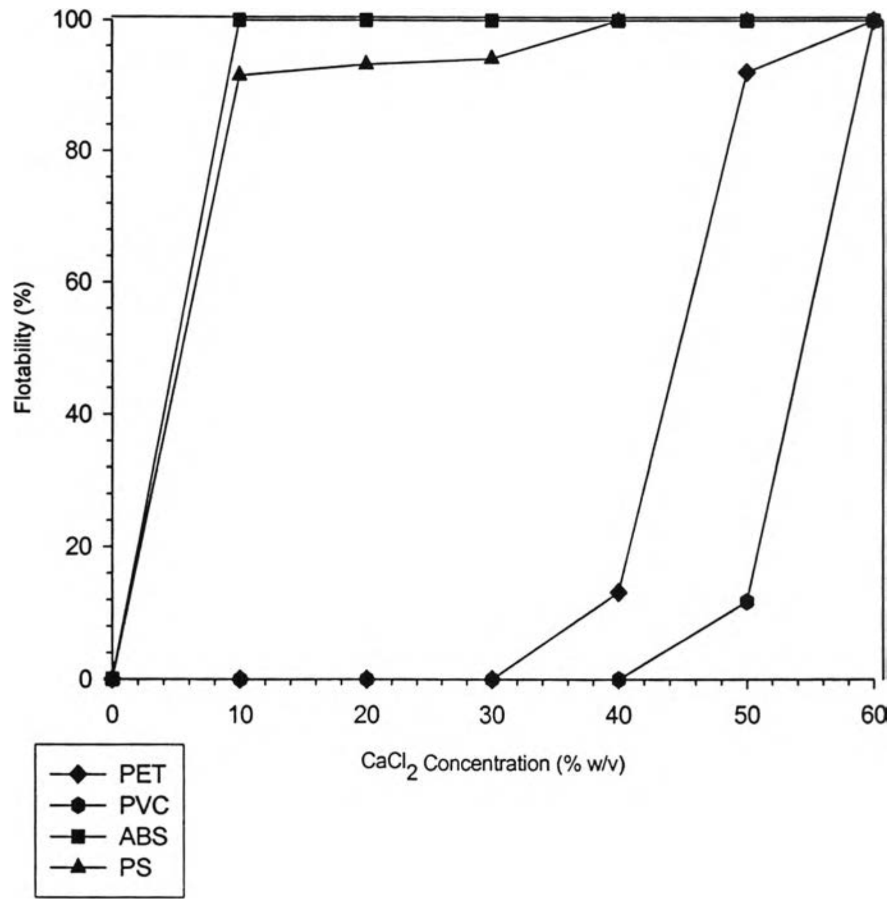

Figure 4.3 The floatability of plastics in the presence of DMS

However, PET/PVC or PS/ABS cannot be separated with high purity by this method because the densities of plastics are too similar. Thus, couple of PET/PVC and PS/ABS were continuing separated by selective flotation method.

Table 4.1 Density of plastics

Plastics	Code	Melting point (°C)	Density (g/cm^3)
PET	1	250 – 260	1.38 – 1.39
HDPE	2	130	0.95 – 0.97
PVC	3	75 – 90	1.20 – 1.42
PP	5	160 – 170	0.90 – 0.91
PS	6	70 – 115	1.05 – 1.07
ABS	7	103 – 128	1.02 – 1.17

Table 4.2 Densities of calcium chloride aqueous solution (DMS) in varied concentration

Concentration of $CaCl_2$ (%w/v)	Density (g/cm^3)
10	1.06
20	1.13
30	1.21
40	1.29
50	1.37
60	1.45

Table 4.3 Densities of ethyl alcohol solution (LMS) in varied concentration

Concentration of Ethyl alcohol (%v/v)	Density (g/cm^3)
10	0.99
20	0.97
30	0.96
40	0.95
50	0.93
60	0.92
70	0.90
80	0.87
90	0.85
95	0.82

4.1.2 Light medium solution

The plastics in Group II, which were floated in water, were separated by ethyl alcohol solution that used as a light medium solution (LMS). HDPE started to separate from PP when using 30 %v/v LMS. Completely separation of HDPE from PP with purity 99.88% and 99.91% recovery for HDPE and recovered plastics purity was 99.90% and 99.64% recovery for PP could be achieved when employing 50 %v/v LMS, as shown in **Figure 4.4**. However, it was obvious that 40 % v/v of ethyl alcohol has density similar to HDPE (**Table 4.1** and **Table 4.3**), thus HDPE was suspended in the solution. It was hard to identify that HDPE was sinking or floating.

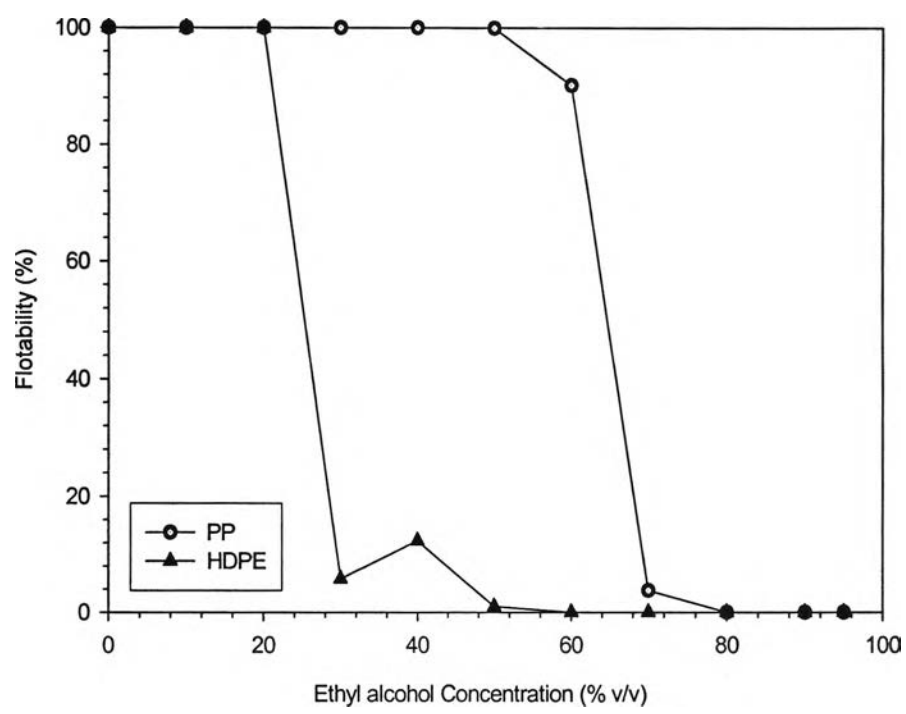

Figure 4.4 The floatability of plastics in the presence of ethyl alcohol solution (LMS)

4.2 Selective flotation technique

4.2.1 PET/PVC

4.2.1.1 The effect of treatment with CaLS wetting agent and pH on the floatability

Figure 4.5 shows the floatability of PET and PVC against a various concentrations of CaLS solution at constant pH 7. One important point to note from this graph is that the decrease of the floatability of PET means that the recovery [a] percentage of PET will increase with the introduction of CaLS. At 500 mg/l CaLS solution gave the highest different of floatability between PET and PVC. Thus, at this concentration was used all the latter tests.

Different from another wetting agent, CaLS could reduce liquid surface tension to minimum value of 55.5 mN/m but the surface tension of CaLS is still much higher than the surface tension of plastics as shown on **Appendix C**. It is obvious that the reduced liquid surface tension was not the main reason for depressing effect of CaLS on plastics because the minimum surface tension of was higher than the solid surface tension of plastics that listed in **Table 2.5**. Therefore, the depressing effect of CaLS on plastics was attributed mainly to its adsorption on the plastics surface. CaLS is a water-soluble polymer with numerous polar groups (S=O and O–H) as shown in **Figure 2.12**. The molecules adsorbed on plastics surface expose some of their polar group oriented towards the aqueous phase, hence making the plastics surface hydrophilic. Especially, dissociated calcium ions might be at the interface between plastics surface and LS because of the electrostatic properly. In addition, electrostatic interaction and van-der-Waals force interaction also can be included since CaLS is anionic polymer.

When varying pH at constant CaLS concentration (500 mg/l), the results showed that pH affected the floatability of plastics as well. PET floatability decreased with decreased in solution pH except at pH 12 **(Figure 4.6)**. At pH that higher than 9, the phenolic hydroxyl in the CaLS molecules dissociates and thus the negative charge of molecule increases strongly (Askvik K.M., *et al.*, 2001). These means, plastics were adequately changed their wettibility by CaLS in alkaline solution. It was especially on PET because in alkaline solution, surface ester linkage in PET was broken up; therefore PET was more hydrophilic by wetting agent and pH.

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[a] The term "recovery" refers to the amount of plastics that could be separated;
Calculating formula of recovery *sees* **Appendix B**

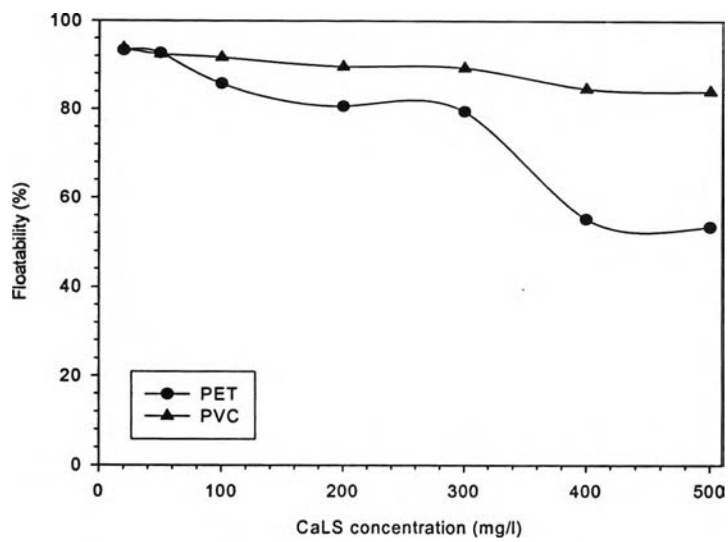


Figure 4.5 Dependence of the floatability of PET and PVC on the varied CaLS concentration at pH 7

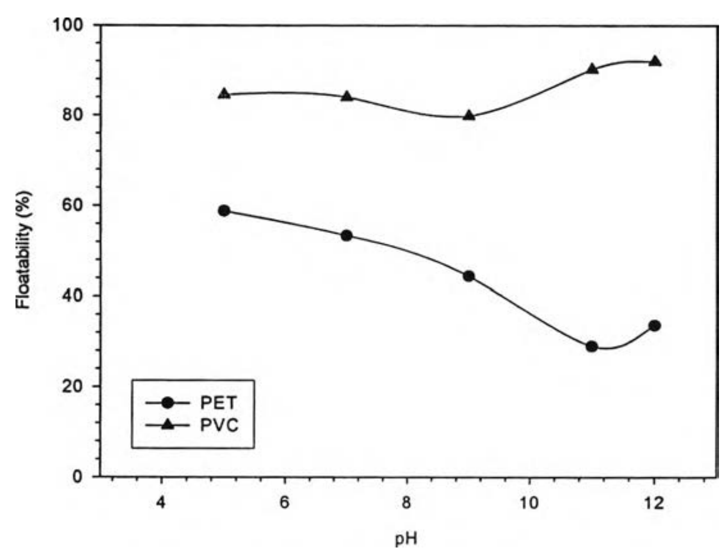


Figure 4.6 Dependence of the floatability of PET and PVC on the varied pH at 500 mg/l CaLS

The differences of the plastics floatability and the potential of separation of plastics by the addition of wetting agents and pH were further verified by the test results of the plastics mixtures. PET and PVC have enough different floatability. They could get almost separated by using CaLS 500 mg/l, pH 11 and mixed PET/PVC for 2 minutes by stirrer then leaved them 2 minutes (2 + 2) for reacting with CaLS, which have purity 87.67% and 76.03%, respectively. This condition was used as criteria for other experiments.

4.2.1.2 The effect of conditioning time on the floatability of plastics

The conditioning time also affected the wettability (reacting time, standing time): 2 + 0.5, 1 + 2, 2 + 3, 2 + 4 and 4 + 2 minute. The parameters were 500 mg/l CaLS and pH 11, which obtained from the section 4.2.1.1. The result was shown in **Figure 4.7** and **Table 4.4**. From theses results, one can see that there is an ideal conditioning time for the wetting agent to act upon the PET. For a conditioning time more than 4 minutes (2 + 2), the CaLS acted upon both PET and PVC, which was not desired. At conditioning time of 4 minutes (2 + 2), PVC recovery was high, therefore, PVC contaminated PET less than 13 %. Thus, the purity of PET and PVC were 87.67% and 76.03% respectively.

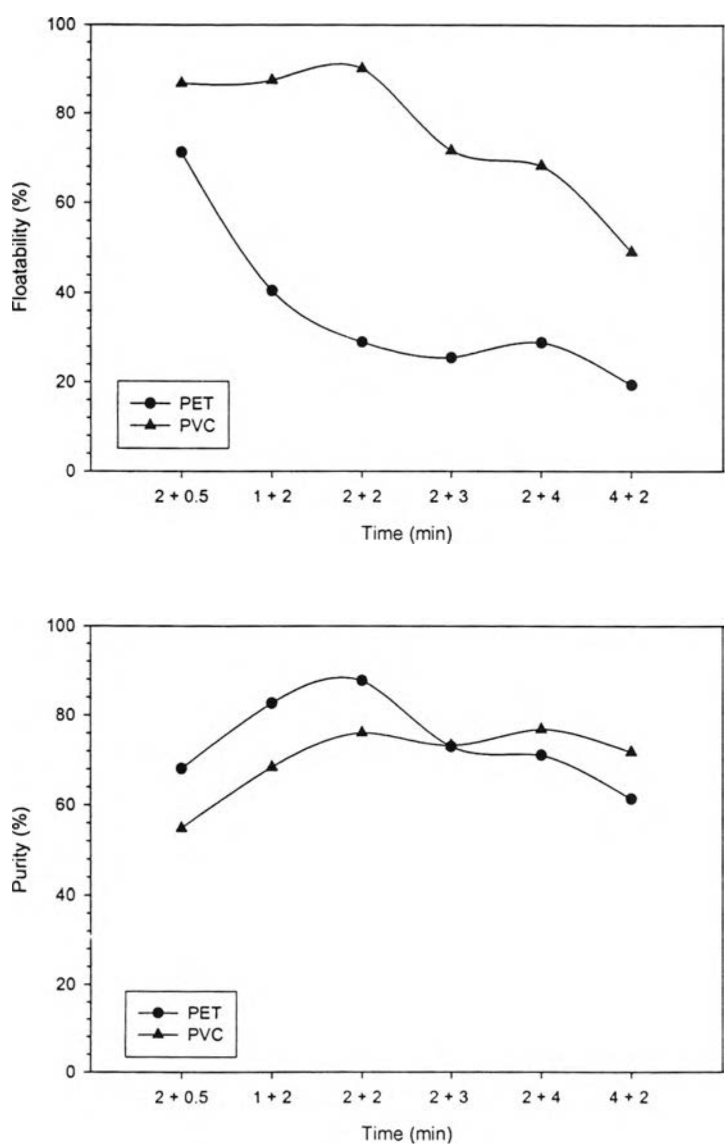


Figure 4.7 Floatability and purity of PET and PVC on the varied time at 500 mg/l CaLS, pH 11

Table 4.4 Flotation experiments results according to conditioning time at 500 mg/l CaLS, pH 11

Conditioning time (min)	PET recovery (%)	Purity of PET recovered (%)	PVC recovery (%)	Purity of PVC recovered (%)
2 + 0.5	28.17	68.04	86.81	54.79
1 + 2	59.53	82.61	87.47	68.37
2 + 2	71.04	87.67	90.19	76.03
2 + 3	74.53	72.98	71.61	73.21
2 + 4	79.16	71.04	68.18	76.83
4 + 2	80.67	61.31	49.10	71.75

4.2.1.3 The effect of varying the concentration of electrolyte on the floatability of plastics

Although, lignosulfonate was an anionic reagent and both PVC and PET were also negatively charged, even in a solution containing calcium. Calcium has two positive charges, might act as a bridge between the wetting agent and surface of the plastics. To prove this assumption, Ca^{2+} as $CaCl_2$ was added in the medium, which is 500 mg/l CaLS, pH 11 and time for conditioning were 1 + 2 and 2 + 2 at various concentrations; 0.1, 0.3, 0.5, 0.7and 0.9 %w/v. **Figure 4.8** and **Figure 4.9** show that cation can improve in the recovery and purity of the plastics. The PET-recovery and purity reach a maximum at 3 minutes conditioning time and 0.1 %w/v $CaCl_2$ at 89.29% and 85.74% respectively. The PVC-recovery and purity were 85.22% and 88.88% respectively at the same condition. The recovery of PET increased when adding more $CaCl_2$ on the other hand, PVC-recovery decreased because Ca^{2+} might be formed complex molecular with CaLS. It made CaLS more adsorbed to the surface of plastics thus, plastics was rendered more hydrophilic and sunk at the bottom of flotation column. The mechanism of this adsorption of reagents on plastics surface has not yet been understood completely. However, there is a possible reason for explanation this phenomenon (**Figure 4.10**). Calcium would thus reduce lowering of surface charge due to lignosulfonate adsorption. Furthermore, the main interactions involved in lignosulfonate adsorption on the plastics are electrostatic (Guern C.LE., *et al.*, 1999). Calcium may also modify the structure of the adsorbed layer by reinforcing loops and bridges between the adsorbed macromolecules, which would mask hydrophobic sites on the plastics surfaces. In parallel, hydrophilic segments of LS may spread in the solution, hydrate and have an effect on bubble repulsion for macromolecular organic depressants likes in sulphide flotation (Pugh R.J., 1989).

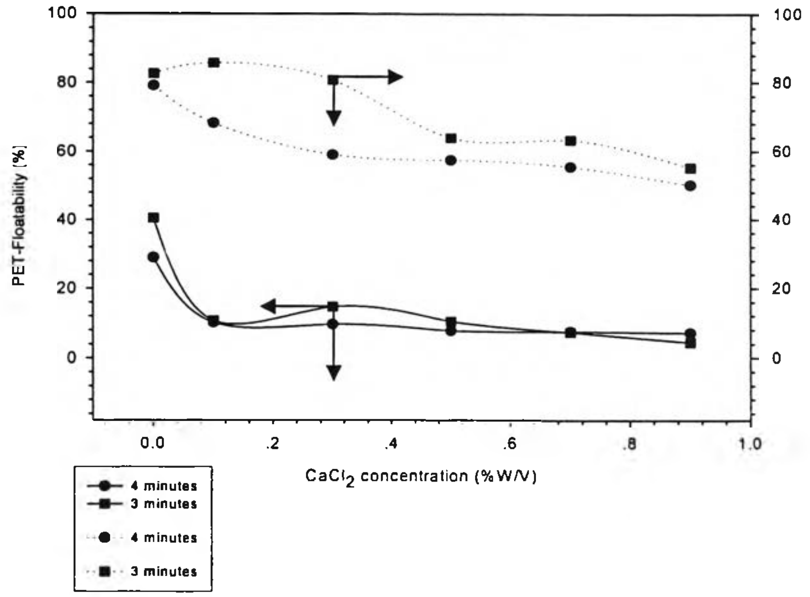


Figure 4.8 The effect of cation on the floatability and purity of PET (using 500 mg/l CaLS, pH 11)

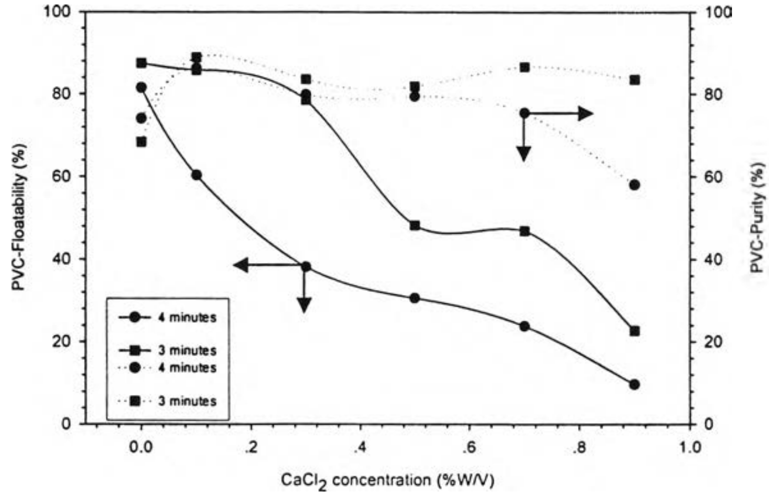


Figure 4.9 The effect of cation on the floatability and purity of PVC (using 500 mg/l CaLS, pH 11)

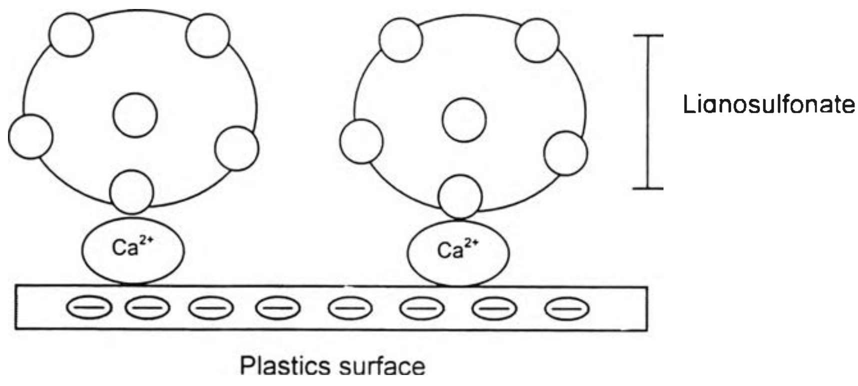
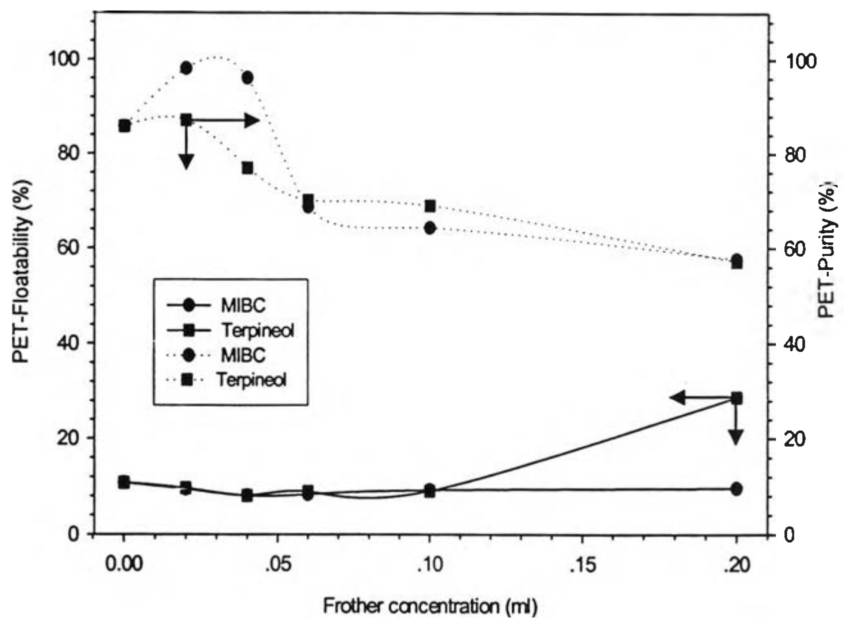


Figure 4.10 The role of calcium in the adsorption mechanism of lignosulfonate on plastics surface (redrew from Guern C.LE., 1999)

4.2.1.4 The effect of frothers and their concentrations on the floatability of plastics

The influence of MIBC and terpineol concentrations of the aqueous medium had on the floatability of the plastics was only tested at the best condition acquired from previous section; 500 mg/l CaLS, pH 11, conditioning time 3 minutes and 0.1% w/v $CaCl_2$. These results are shown in **Figure 4.11**. It is seen that for a wide range of frothers, from 0.02 – 0.2 ml, the floatability of PET was slightly affected. Moreover, it was clear that the frothers' concentration would not significantly improve the recovery percentage of PET. On the other hand, frothers were influential on the increasing floatability of PVC, thus the purity of recovered PET decreased when concentration of frothers increased.

In order to achieve the highest recovery percentage and purity of recovered PET and PVC, the medium solution was 500 mg/l CaLS, pH 11, 0.1% w/v CaCl2, 0.02 ml MIBC and conditioning time was 3 minutes. PET and PVC were recovered 90.57% and 98.17% with purity 98.05% and 91.15%, respectively.



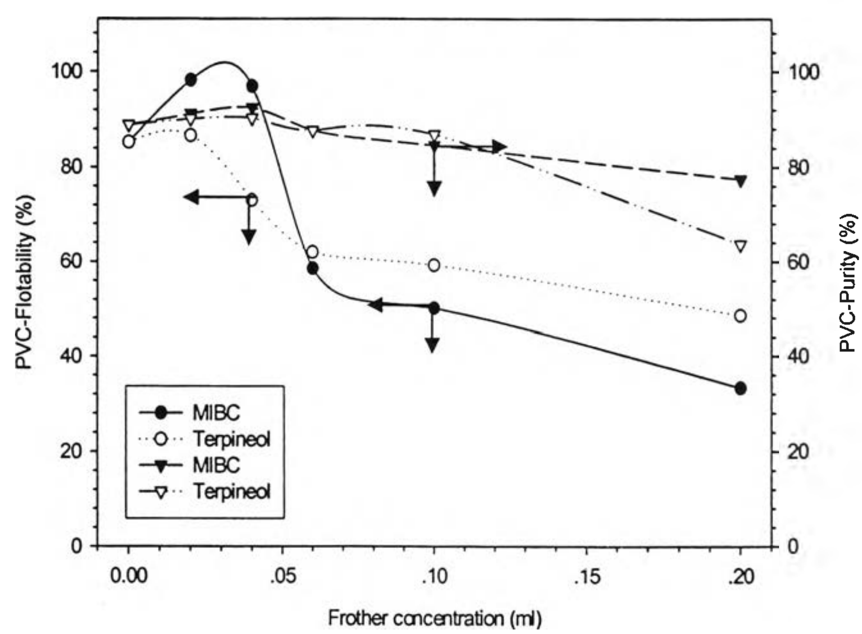


Figure 4.11 The concentrations of frother reagents (MIBC and terpineol) as function of separation PET and PVC

4.2.1.5 The effect of height of flotation cell on the floatability of plastics

Table 4.5 shows the result of effect of flotation column height. Increasing in column height from 38 to 60 cm decreased the floatability of PVC and contaminated PET, which depressed at the bottom of the column. Moreover, higher flotation column 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 (PVC) still contaminated with hydrophilic plastics (PET).

Table 4.5 Flotation experiments results according to height of flotation column

Column height (cm)	PET recovery (%)	Purity of PET recovered (%)	PVC recovery (%)	Purity of PVC recovered (%)
38	90.53	98.05	98.17	91.15
60	90.37	86.35	85.68	89.87

4.2.2 PS/ABS

4.2.2.1 The effect of treatment with CaLS wetting agent and pH on the floatability

From the preliminary test, water as medium solution that used in part of PET/PVC separation was not effective in this experiment because the densities of plastics (ABS and PS) were similar to water. Only wetting agent could not completely separate plastics mixture to individual. Therefore, medium solution density must be modified and 20 %v/v of ethyl alcohol was found that it had a suitable density (0.98 g/cm^3) for separated ABS/PS. Thus, for ABS/PS separation, the medium solution was 20 %v/v of ethyl alcohol.

The PS/ABS mixture was treated with CaLS at concentrations in range of 20 – 500 mg/l and the pH of solutions were 5, 7, 9, 11 and 12. **Figure 4.12** shows the floatability of ABS and PS as the concentration of CaLS was varied. CaLS could render PS more hydrophilic when concentration of wetting agent was increasing. In case of ABS, firstly, low concentration of CaLS (≈ 200 mg/l) decreased the ABS flake's floatability, as it became less hydrophobic. Following this, the froth layer in the flotation column gradually stabilised, while the concentration of CaLS was increased (up to 400 mg/l). Therefore, floatability of hydrophobic ABS flakes was higher due to the fact it could be capture by the froth layer. PS floatability started going down when using 300 mg/l CaLS at pH 7. Moreover, recovery and recovered plastics purity have a slightly increased, while increased concentration of CaLS from 200 mg/l to 300 mg/l. Hence, taking into consideration environmental problems and cost effective, 200 mg/l CaLS was better and chosen as the standard for all latter experiments.

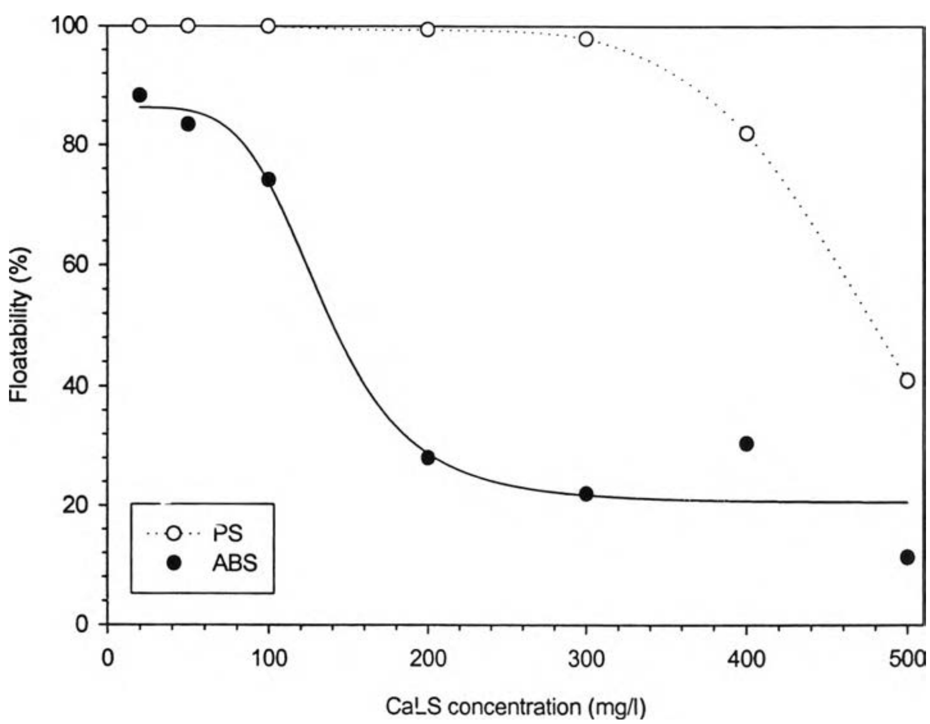


Figure 4.12 Dependence of the floatability of ABS and PS on the varied CaLS concentration at pH 7

Significant effects of pH were observed during the flotation experiments. The result is shown in **Figure 4.13**, it seem that pH did not affect on PS because PS still hydrophobic, while level of pH was being changed. On the other hand, effect of pH on ABS could not be a trend. Although, CaLS was well deionised in alkaline solution but the results shows in neutral solution can achieve the high purity of individual plastics. It might be the chemical structure of ABS and PS. ABS and PS has apolar C–H groups dominate in the molecular structures and they are very hydrophobic, whereas other plastics such as PET or PVC, they have C=O and C–Cl, respectively in their molecules. Theses groups are polar, which may be more sensitively to pH than apolar group. The difference in percentage of floatability of ABS and PS was at pH 7. Hence, a pH 7 was selected as the standard level for all subsequent experiments.

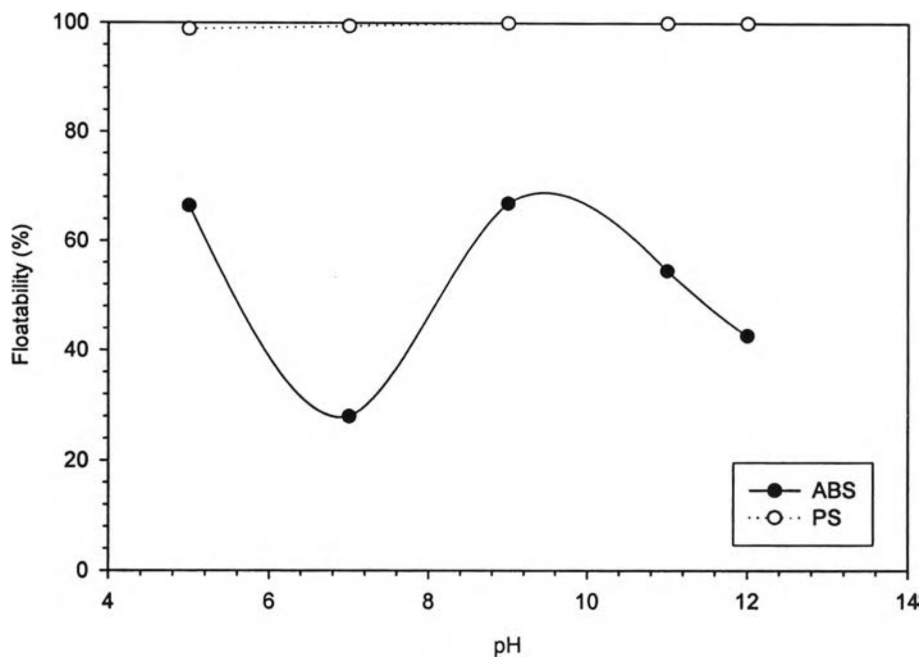


Figure 4.13 Dependence of the floatability of ABS and PS on the varied pH at 200 mg/l CaLS

It seems that ABS and PS can be separated from each other by 200 mg/l CaLS at pH 7. The recovery and recovered ABS purity reach 72.04% and 99.17%, respectively. In addition, the recovery and recovered PS purity attain 99.41% and 78.22%, respectively. However, recovery percentage of ABS and purity of recovered PS will be improved.

4.2.2.2 The effect of conditioning time on the floatability of plastics

The process of experiment was as same as section 4.2.1.2. The medium solution was treated with 200 mg/l CaLS, pH 7. **Figure 4.14** shows long conditioning time (more than 5 minutes) were affected both of ABS and PS and induced them to more hydrophilic, which was not desirable. However, if looked at the recovered plastics purity, conditioning time for 4 minutes or 5 minutes was not much different about 99.17% and 97.89%, respectively for ABS and 78.22% and 79.65%, respectively for ABS. Hence, Conditioning time for 4 minutes was selected as the criterion for all subsequent experiments.

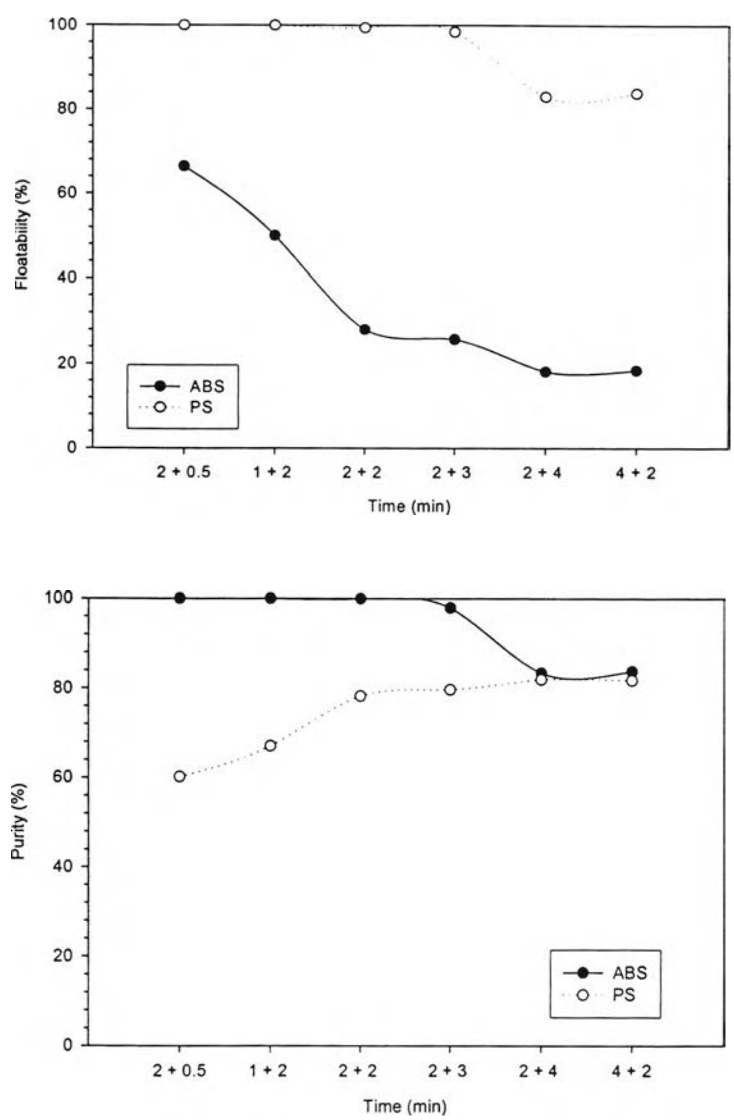


Figure 4.14 Floatability and purity of ABS and PS on the varied time at 200 mg/l CaLS, pH 7

4.2.2.3 The effect of varying the electrolyte concentration on the floatability of plastics

The consequences of the experiment at results were shown in **Figure 4.15**. It referred to the diagram, electrolyte (Ca^{2+}) can induce both ABS and PS to hydrophilic in the even that added $CaCl_2$ through the medium in high concentration (> 0.5% w/v). Even though, a few concentration of $CaCl_2$ (≈ 0.1% w/v) made only ABS too more hydrophilic but affected PS slightly not. In this stage, the recovery p ercentage and recovered ABS purity increased to 96.28% and 98.97%, respectively, moreover 99.01% and 96.43%, respectively for PS.

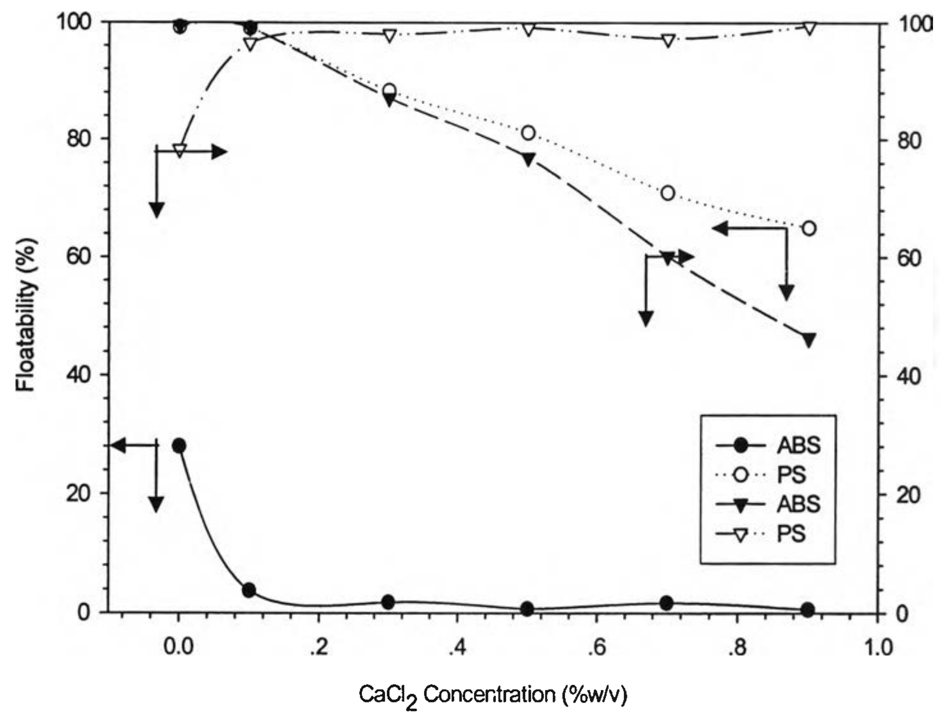


Figure 4.15 The effect of cation on the floatability and purity of ABS and PS (using 200 mg/l, pH 7 and 4 minutes conditioning time)

4.2.2.4 The effect of frothers and their concentrations on the floatability of plastics

Figure 4.16 shows the effect of MIBC on the floatability of plastics, MIBC did not improve the floatability of ABS and PS. Furthermore, high volume of MIBC behaved as if a wetting agent on PS. It rendered PS more hydrophilic. In case of terpineol, PS was not affected by terpineol at any concentration **(Figure 4.17)**. Terpineol helped ABS floating to the top of the column at intermediate volume (approximate 0.6 ml) but at the high concentration of terpineol depressed PS as wetting agent. Thus, frother was not much necessary to ABS/PS separation by flotation technique.

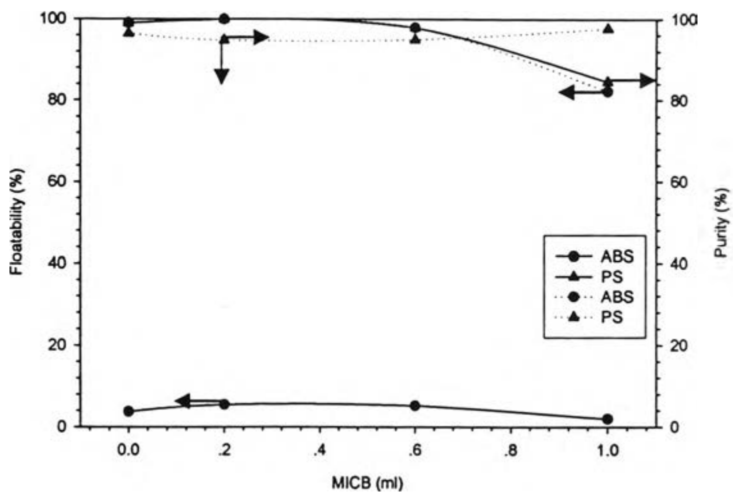
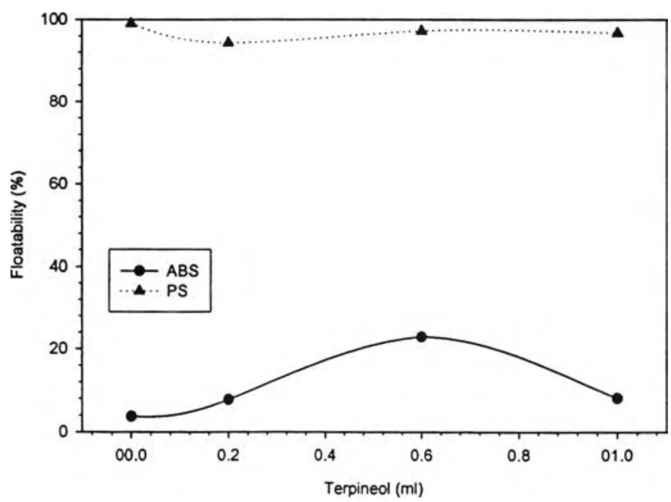


Figure 4.16 The concentration of MIBC as function of ABS/PS separation



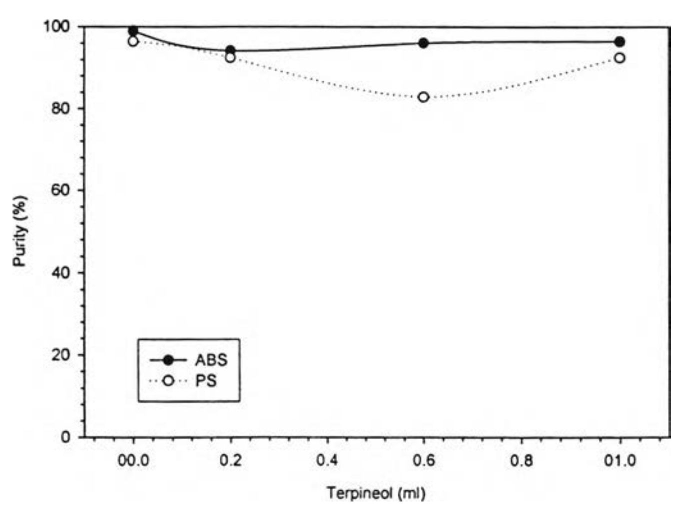


Figure 4.17 The concentration of terpineol as function of ABS/PS separation

4.2.2.5 The effect of height of flotation cell on the floatability of plastics

Table 4.6 shows the results of the experiments, high column obstructed the floating of plastics. If the cohesion force of plastics and air bubble was not strong enough, the plastics could not completely float through the top of the column. Moreover, it must have more the medium solution in high column, which extended the cost of the separation.

Table 4.6 Flotation experiment results according to height of flotation column

Column height (cm)	ABS recovery (%)	Purity of ABS recovered (%)	PS recovery (%)	Purity of PS recovered (%)
38	96.28	98.97	99.01	96.43
60	60.42	95.48	97.10	70.77

Furthermore, these percentages of plastics recovery and recovered plastics purity of all this experiment were relatively high when compared with previous works as shown in **Table 4.7**.

Table 4.7 The comparison of plastics recovery and recovered plastics purity

Plastics	Wetting agent (mg/l)	Plastics recovery (%)	Recovered plastics purity (%)	Literature
PET/PVC	CaLS (500)	PET = 98.17 PVC = 90.57	PET = 91.15 PVC = 98.05	This work
PET/PVC	Gelatine solution (45)	PET = 75 PVC = N/A	PET = 99.8 PVC = N/A	Jordan, C.E., (1992)
PET/PVC	20% Methanol	PET = 0 PVC = 92	PET = 0 PVC = 99.50	Buchan, R., (1995)
PS/ABS	CaLS (200)	PS = 99.01 ABS = 96.28	PS = 96.43 ABS = 98.97	This work
PS/ABS	Methyl cellulose (57.14)	PS = 11.40 ABS = 96.40	PS = 76.00 ABS = 52.11	Shen, H., *et al.* (2002)

4.3 Contact angle measurement

The contact angle was measured for supporting and proving the results of the experiments. Normally, plastics are hydrophobic materials in nature. **Table 4.8** shows the contact angle of plastics in water, which was measured in this work by tensiometry.

Table 4.8 Contact angles of plastics with water

Plastics	Contact angle (deg)	
	This work	Other works
PS	88	86.3 [a]
ABS	89	83.7 [a]
PVC	80	84.6 [a]
PET	78	76.5 [b]

[a] from Fraunholez N., 1997 by Axisymmetric drop shape analysis technique

[b] from Dodbiba N., *et al.*, 2002 by Axisymmetric drop shape analysis technique

However, CaLS could change the wettability (contact angle) of plastics to less hydrophobic or hydrophilic materials as shown in Figure below. **Figure 4.18** shows reduction of contact angle of PET and PVC when concentration of CaLS was increasing. Therefore, PET and PVC was more hydrophilic in higher CaLS concentration. At 500 mg/l CaLS, pH 11, contact angle of PET was in range of hydrophilic zone while, PVC was still in hydrophobic zone. The difference of contact angle between PET and PVC was about 5 degree that enough to separated these plastics individually. Moreover, this result was consistent to the results of prior experiments that found out 500 mg/l CaLS, pH 11 was the optimal condition for separating PET/PVC. This supported the result in section 4.2.1.1.

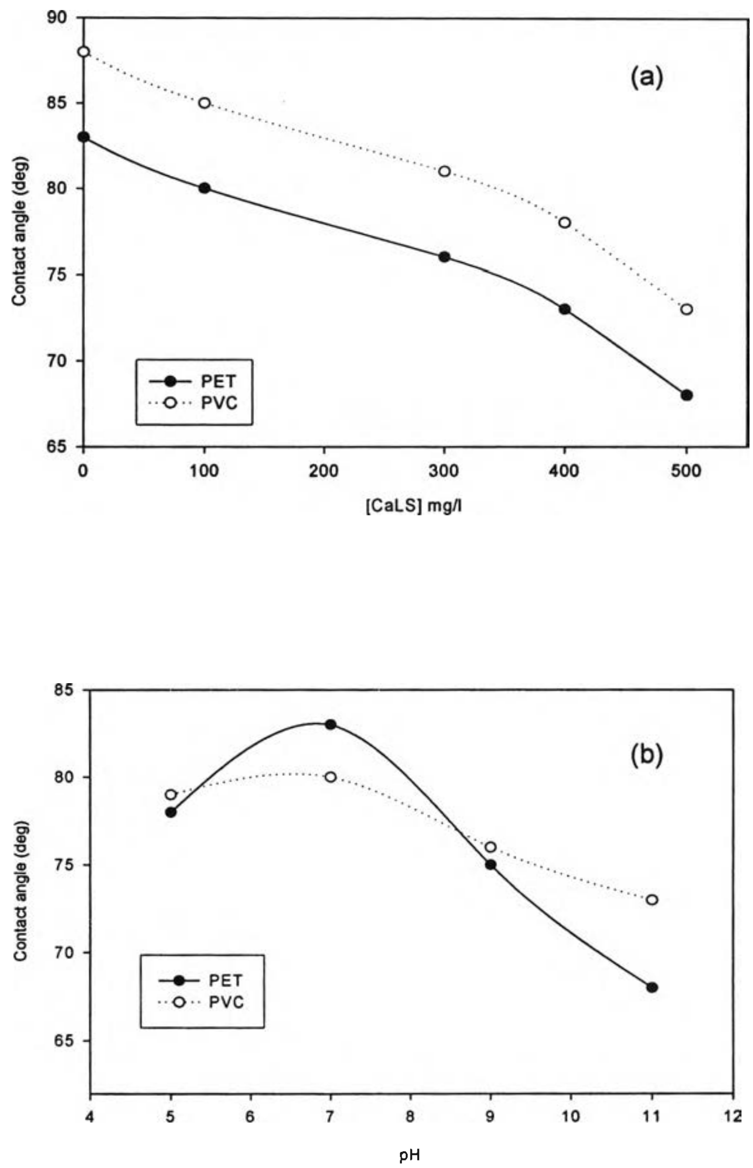


Figure 4.18 Contact angle of PET and PVC with different concentrations of CaLS and pH (a) at pH 11 varied CaLS concentrations (b) at 500 mg/l CaLS varied pH

In case of ABS and PS, the results were similar to PET/PVC. **Figure 4.19** shows contact angle of ABS and PS at various concentrations of CaLS. ABS and PS were more hydrophilic when the concentration of CaLS increased and at pH 7, the contact angle of ABS and PS were most different. Moreover, this contact angle also supported the results in the section 4.2.2.1.

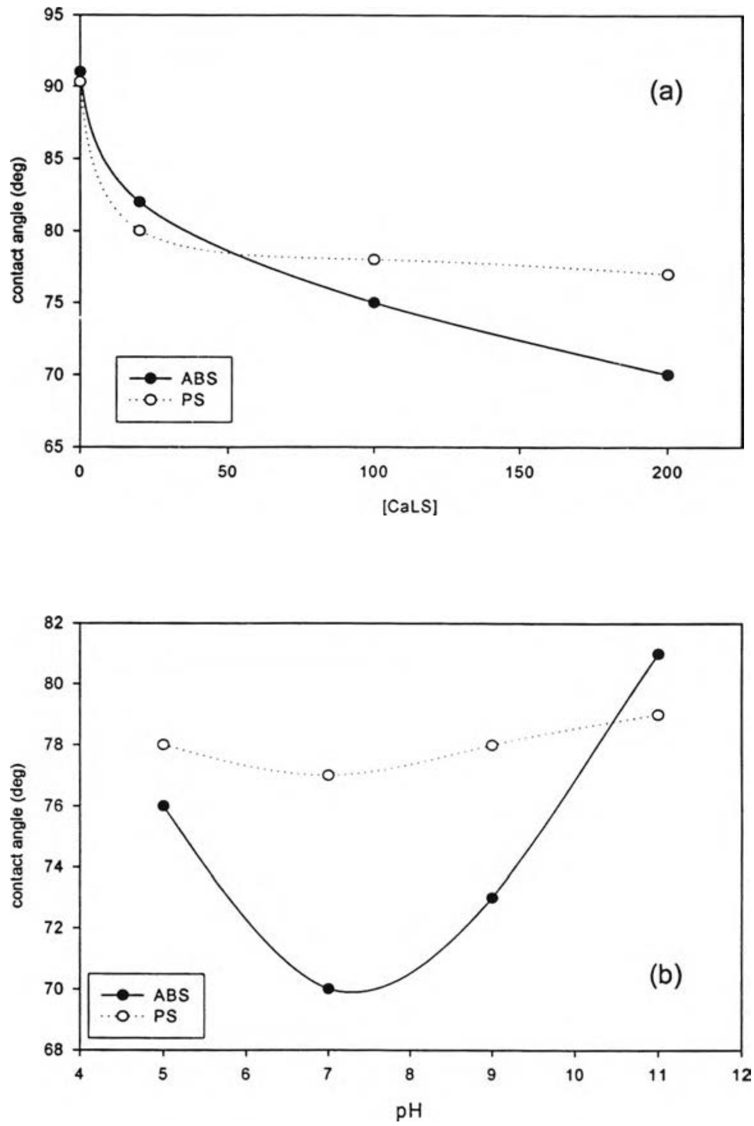
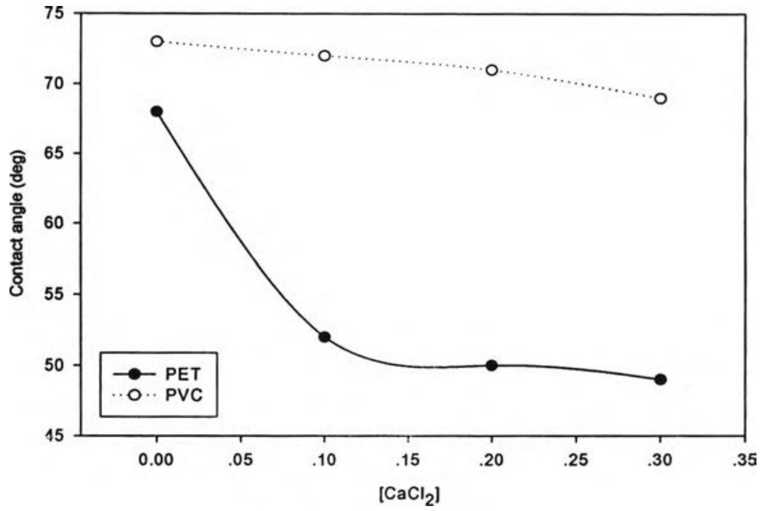


Figure 4.19 Contact angle of PS and ABS with different concentrations of CaLS and pH (a) at pH 7 varied CaLS concentrations (b) at 200 mg/l CaLS varied pH

Electrolyte, especially bivalent cation, can induce plastics too more hydrophilic than only using wetting agent. According to **Figure 4.20**, contact angle of plastics decreased when increased C aLS c oncentration. T his r esult w as i n t he l ine o f s ection 4 .2.1.3 and 4 .2.2.3.



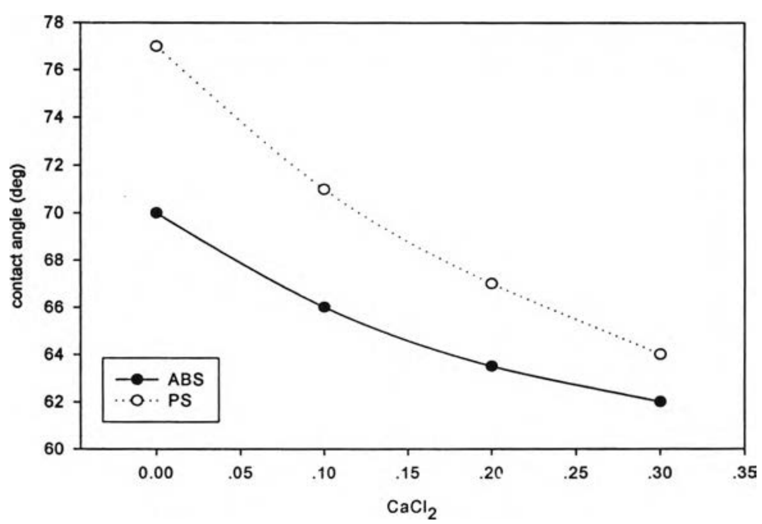


Figure 4.20 Contact angle of plastics with deferent concentrations of $CaCl_2$

4.4 Assessment of application of chemical conditioning method in plastics flotation

Chemical conditioning is a process in which the adsorption of wetting agents on the plastics surface lead to a decrease in hydrophobicity of the solid-liquid interface (Shen H., 1999). Besides the wetting agent CaLS, there are other commonly used wetting agent, such as methyl cellulose, quebracho, tannic acid and so on. These reagents have been widely used as organic depressant in mineral processing. There are stable, non-toxic and inexpensive with a wide resource. In addition, according to the results above, the concentration of CaLS in the flotation media for selective flotation separation of the plastics mixtures are 200 and 500 mg/l. They are equivalent to the dosages of 12 – 300 g CaLS per ton of solid feed when the solid: water is 1: 6 by weight in the industrial flotation process. Thus the assumption of the wetting agent for flotation separation of plastics mixtures is low. Therefore, chemical conditioning with wetting agents is practical and cost-effective.