Separation of PVC from PET/PVC Mixtures Using Flotation by Calcium Lignosulfonate Depressant

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Abstract. Recycling is an important activity in the minimization of waste that results from human activities. In the United States, 103.2 billion pounds of plastic are produced in 2011. Unfortunately, the majority of this plastic ends up in landfills where its decomposition process can take anywhere from 10 to 30 years. In this work, froth flotation was used to treat PVC (polyvinyl chloride) and PET (polyethylene terephthalate) mixtures. The parameters studied are fed mixtures component ratios, concentration of Calcium Lignosulfonate as wetting reagent and a number of cleaning flotation. The results show a yield of 100% pure PVC separated from PET.

Keywords: Separation, flotation, polyethylene terephthalate, polyvinyl chloride, calcium lignosulfonate, depressant.
1. Introduction

In worldwide, the total plastics consumption will have an average growth rate of 5%-6%, and to reach 297.5 million tonnes by 2015. Asia has been world’s largest plastics consumer for several years, accounting for about 30% of the global consumption excluding Japan, which has share of about 6.5%. Next to Asia is North America with 26% share, then Western Europe with 23% share in the global market [1].

As the Plastics-the Facts 2011 reports, from 2009 to 2010 the global plastic production of plastics increased by 15 million tonnes or 6% to 265 million tones, confirming the long term trend of plastics production growth of almost 5% per year over the past 20 years. In 2010 Europe accounted for 57 million tonnes (21.5%) of the global production and China overtook Europe as the biggest production regional at 23.5% [1].

In the United States, 103.2 billion pounds of plastics are produced in 2011. Unfortunately, the majority of this plastic ends up in landfills where its decomposition process can take anywhere from 10 to 30 years.

To recycle plastic waste, it is necessary to separate the plastics from each other. Plastics having different density can be easily separated, while quite difficult for the separation of PET and PVC which have similar density (1.30 g/cm³ for PET, and 1.5 g/cc³ for PVC). Various studies on the PET and PVC separation have been employed. Nakajima, J. et al. (1999) initially reported the removal of PVC from PET/PVC mixtures by air separation [2]. Carlini, et al.(1995) investigated the separation of PET from PET/PVC mixtures by means of differential thermal behaviors of the both plastics [3]. De Haan, et al.(1997) assessed the technical feasibility of the electrostatic separation of PET and PVC [4]. Yoneda, et al. (1998) indicated that PET bottles and PVC bottles could be identified respectably by the IR data of adsorption wavelength; therefore it might be possible to separate the PET bottles from the PVC bottles [5].

The development of flotation for plastic waste recycling aims at producing a new substitute material for virgin plastic as well as minimizing pollution and the environmental impact caused by inappropriate disposal.

PET is currently the major recyclable plastic material, followed by high-density polyethylene(HDPE), poly-propylene (PP), and polyvinyl chloride(PVC). New products and end-use markets are developing rapidly for these materials. A few examples include fibers, moldings, construction materials, chemical intermediates, blending components, etc. [6].

Flotation was originally developed for ore separation in the beginning of the 20th century. The application to flotation separation of plastic mixtures is relatively new. The earliest publication on this subject dates back only to the seventies. The idea to apply this technique to plastic separation resulted from flotation research, which demonstrated that the surface properties of different materials could be altered selectively by surfactant adsorption [6].

Flotation systems include all three phases of matter—liquid, solid, and gas. A pulp (a mixture enters a flotation device where the gaseous phase is added. The principle of flotation technology is making, selectively, hydrophobic(water repellent) materials surfaces (either presenting natural or induced hydrophobicity) to come in contact with gaseous bubbles, thus creating the opportunity to aggregate gas bubbles onto the hydrophobic particles. These bubble-particle aggregates are transferred into a froth phase generally formed on the top of the flotation machines. The froth carrying the selected bubble-particle aggregates is removed as one of the products of a given flotation operation. The particles remaining in the pulp (hydrophilic) are discharged by an appropriate mechanism [7].

Selective flotation of plastics needs the selective wetting of one of the components. Wettability of hydrophobic surfaces can be achieved through the action of surfactants or depressants. Separation by flotation is based upon selective attachment of bubbles on the particles to be separated. This requires a sufficient difference in the wettability of the particle surfaces [8]. Since in their natural state most plastics are hydrophobic, selective wetting of one or more components is necessary for the separation. As plastics belong to low-energy-surface solids, wetting by water can be achieved through the addition of an appropriate reagent. Suitable surfactants of plastics are composed of molecule capable of adsorbing on plastic surfaces as well as of molecular groups that render the particles hydrophilic [9].

surfactant adsorption resulted in a synergetic effect with improved separation and lower reagent consumption[14]. This happens because the alkaline treatment promotes the hydrolysis of the polyester particles surface, increasing the number of hydrophilic groups (hydroxyl and carboxyl) and surface roughness [13].

To succeed in a separation of mixed polymers based on polymer type using selective flotation, it is necessary to render one surface more hydrophilic while the others are still in a hydrophobic state. The hydrophilic one remains in the flotation solution while air bubbles are attaching to hydrophobic one. Selective flotation for separation of mixed polymers is controlled not only by surface chemistry based on the different wettability characteristics of polymers but also by shape and size of polymers in waste [18-21].

In the present work, a treatment of PVC and PET particles with alkaline solutions followed by selective froth flotation using Calcium Lignosulfonate as wetting agent has been developed and tested on a laboratory scale. The investigated parameters studied are concentration of CaLS, conditioning time, fed pseudo mixtures and a number of cleaning flotation.

2. Experiment Method and Materials

The samples of 2 different kinds of plastics wastes were Polyvinyl Chloride (PVC) and Polyethylene Terephthalate (PET). The samples were post-consumer plastics and obtained from vellums and drinking bottles respectively. PVC and PET flakes used in this study were prepared by shredding into small pieces having size 5x5 mm and thickness 0.3 mm using a cutter for plastic. The density of the used PVC and PET flakes was 1.24 and 1.33 g/cm$^3$ respectively. All plastic flakes were washed organic contaminations in alkaline treatment by NaOH 20 minute at the range of pH 11-12 and temperature 60$^\circ$C and rinsed with tap water as shown in Fig. 1. Three groups of pseudo mixtures were prepared by mixing the PVC and PET flakes at volume ratios of 75:25, 50:50, and 25:75, respectively. The PVC content in each group of the pseudo mixtures is 74%, 48% and 24% by weight, respectively. The samples used for the tests were of different colors (PVC red and PET green) which made it easier to analyze the concentrate samples through manual sorting at the end of each experiment. The samples used for each test consisted of 100 pieces of plastic.

Flotation reagents used in this study was calcium lignosulfonate (commercial grade CaLS) as wetting agent. Frothing agent was pine oil (commercial grade terpineol). NaOH was used to adjust pH of solution. Tap water was used throughout the experiments.

The flotation experiments were carried out in 4,000 cm$^3$ Denver mechanical flotation machine as shown in Fig. 2. The impeller speed was set at 1100 rpm.

To get an appropriate concentration of wetting agent. The PVC and PET flakes at volume ratios of 50:50 were treated with CaLS at various concentrations (5, 7.5, 10, 12.5, 15 mg/l) for 20 minutes with the range of pH 11-12 and conditioning time of treating plastics with wetting agent was varied at 10, 15, 20 and 25 minutes with the range of pH 11-12 and 7.5 mg/l CaLS for figure out an appropriate time reaction. Finally, an optimal concentration of CaLS solution for separating the plastics waste was found out.

Fig. 1. Alkaline treatment and rinsing of plastic flakes.
The wetting agent when used in plastic flotation adsorbed depressant molecules selectively influence the affinity of bubbles for different types of plastic under appropriate conditions. The frothing agent used was pine oil. Ten drops of frothing agent were used in each experiment. Both conditioning and collection time was about 20 min. Figure 3 shows a simplified process of PVC and PET separation in batch type flotation cell. At first stage of flotation, usually called “Rougher Flotation”, a pseudo mixture containing 100 pieces of plastic flake was fed into flotation cell with water filled, followed with addition of CaLS as a wetting agent, and then stirred, usually called “Conditioning”, for 20 minutes. At this stage, most of the PET flakes gradually sunk while the PVC flakes floated to the top of the flotation cell. PVC content in the floated portion was counted while the sunken portion was removed. Then, the floated portion was fed into the same flotation cell for re-flotation in order to increase the PVC content. This stage is usually called the 1st cleaner stage. If the PET flakes still contaminate in the floated portion, the next cleaner stage and so on, the 2nd cleaner and/or the 3rd cleaner process, should be operated until obtaining the maximum PVC content.

![Diagram of separation process](image-url)

Fig. 3. Simplified diagram for separation of PET and PVC.
3. Results and Discussion

Both plastics were found to be naturally floatable (hydrophobic). Therefore, it was necessary to use an appropriate surfactant to achieve selective separation. The flotation cell usually provides the sample fed into the cell with their gravity and buoyancy force of air bubbles. Plastic particles are naturally hydrophobic and are therefore amenable to be separated by flotation. Unfortunately, separation of plastic particles is difficult unless the other components are rendered hydrophilic. In this case, PET readily adsorbed the CaLS wetting agent better than PVC. As a result, by selective adsorption onto the PET particles, it is possible to change PET’s hydrophilic / hydrophobic properties while the PVC remains virtually unaffected. Under these conditions, the PET surface will be rendered hydrophilic while the PVC will remain hydrophobic. When PET is impregnated with CaLS, separation from PVC is possible by bubbling air through a suspension of the plastic flakes in water. Air bubbles have a high affinity for water repellent surfaces. This selectivity allows air bubbles to preferentially attach to the PVC flakes, while the PET flakes show a low affinity. Consequently, the PVC floats while the PET sinks (Fig. 4).

Fig. 4. Simplified mechanism for separation of PET and PVC.

Figure 5 shows the floatability of PVC and PET against a various concentrations of CaLS solution at the range of pH 11-12 and conditioning time 20 minutes. One important point to note from this graph is that the decrease of the floatability of PET with the introduction of CaLS. The CaLS acted upon both PET and PVC with the concentration more than 12.5 mg/l. At 10-12 mg/l CaLS solution gave the optimum different of floatability between PVC and PET. Thus, at this concentration was used all the latter tests.
Fig. 5. Dependence of the floatability of PVC and PET on the varied CaLS concentration at pH 11-12 and conditioning time 20 minutes.

Fig. 6. Dependence of the floatability of PVC and PET on the varied conditioning time at pH 11-12 and 7.5 mg/l CaLS concentration.

The conditioning time also affected the wettability: 10, 15, 20 and 25 minutes. The constant parameters were 7.5 mg/l and pH 11-12 which obtained from Figure 5. The result was shown in Fig. 6, one can see that the decrease of the floatability of PET with the increase of conditioning time. At conditioning time of 20 minutes gave the highest different of floatability between PVC and PET. Thus, at this concentration was used all the latter tests.

The floatability behavior of the samples is graphically represented as the PVC recovery and the purity of PVC recovered in each flotation stage. Graphical representations also indicate the relationship of the PVC recovery, the purity of PVC recovered and wetting agent concentration. Figure 7 shows the relationship of the PVC recovery as well as the purity of PVC recovered at each flotation stage of the 50:50 pseudo mixtures. It was found that the purity of PVC recovered gradually increased at each flotation stage when using 7.5 mg/l CaLS concentration, while constant at 100% recovery. At 2nd Cleaner stage gave the complete of separation between PVC and PET.
Fig. 7. PVC recovery and purity of PVC recovered as a function stage of flotation at 7.5 mg/l CaLS concentration and PVC feed content 48%.

Figure 8 shows the relationship of the PVC recovery as well as the purity of PVC recovered at each flotation stage of the 25:75 pseudo mixtures. It was found that the purity of PVC recovered gradually increased at each flotation stage when using 7.5 mg/l CaLS concentration, while constant at 100% recovery. At 3rd Cleaner stage gave the complete of separation between PVC and PET.

Figure 9 shows the relationship of the PVC recovery as well as the purity of PVC recovered at each flotation stage of the 75:25 pseudo mixtures. It was found that the purity of PVC recovered gradually increased at each flotation stage when using 7.5 mg/l CaLS concentration, while constant at 100% recovery. At 4th Cleaner stage gave the complete of separation between PVC and PET.

Fig. 8. PVC recovery and purity of PVC recovered as a function stage of flotation at 7.5 mg/l CaLS concentration and PVC feed content 24%.
4. Conclusion

The flotation tests showed that the parameters that determine the efficiency of flotation are fed mixtures component ratios, concentration of wetting reagent and a number of cleaning flotation. It was possible to separate PVC from PET through flotation using Calcium Lignosulfonate (CaLS) as a surfactant for PET and pine oil as frothing agent. Results of the study can be summarized as follows.

For the fed pseudo mixtures having 75:25 volume ratio of PET/PVC or having 74% by weight of PET content, the best separation or maximum PVC recovery was achieved when using 7.5 mg/l CaLS concentration at the 4th stage of cleaning flotation. At this condition, both the PET recovery and the purity of PVC recovered were 100%.

For the fed pseudo mixtures having 50:50 volume ratio of PET/PVC or having 48% by weight of PET content, the best separation or maximum PET recovery was achieved when using 7.5 mg/l CaLS concentration at the 2nd stage of cleaning flotation. At this condition, both the PVC recovery and the purity of PVC recovered were 100%.

For the fed pseudo mixtures having 25:75 volume ratio of PET/PVC or having 24% by weight of PET content, the best separation or maximum PVC recovery was achieved when using 7.5 mg/l CaLS concentration at the 3rd stage of cleaning flotation. At this condition, both the PVC recovery and the purity of PVC recovered were 100%.

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References


