SELECTIVE FLOTATION OF POLYVINYL CHLORIDE (PVC)/ POLYETHYLENE TEREPHTHALATE (PET) MIXTURES

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ABSTRACT

Recycling is an important activity in the minimization of waste that results from human activities. Once plastics enter the consumer market, recycling becomes considerably a necessity. Before polyvinyl chloride (PVC) and polyethylene terephthalate (PET) water and soft-drink waste bottles can be recycled, it is necessary to separate these two materials. As PVC and PET have similar densities, froth flotation was adopted as an alternative to conventional density-based separation techniques. In view of froth flotation being mainly based on wettability differences and both plastics being naturally hydrophobic, a sodium and calcium and magnesium lignosulphonate were selected to render PET hydrophilic and cause its depression. Static contact angle measurements and microflotation tests were carried out.

Based on the results obtained through contact angle measurements, the best condition of selectivity between PET and PVC was observed using calcium lignosulphonate at concentration level of 300 mg/L, presenting 78.6° for PVC and 49.3° for PET

The best flotation results showed that 90.6% recovery of PET can be obtained while rejecting almost all PVC (97.2%) using calcium lignosulphonate as depressant at a concentration level of 500 mg/L in the presence of $Ca^{2+}10^{-3}$ mol/L.

INTRODUCTION

The production of plastics has grown significantly in the United States in the last several years (26 million tons in 1998) with annual growth rate of about 10%. By the year 2000, plastic production was predicted to increase by about 50% to almost 41 million tons (Drelich et al., 1998).

Recycling post-consumer plastic wastes is quite new in the United States. At the beginning of the 1990s, only about 1% of the post-consumer plastic waste stream was recycled.

Up to now, a great portion of plastic waste is either landfilled or incinerated with municipal solid waste. Landfilling and incineration of municipal solid waste becomes more expensive and in many instances these methods of disposal are no longer acceptable.

In view of the problems associated with the safe disposal of plastic waste, the efforts are being made to find efficient ways of recycling this waste. The development of mineral technologies applied to plastic waste recycling has the aim of producing a new substitutive material for the virgin plastic besides minimizing pollution and environmental impact.

In most cases, plastic wastes are composed of four groups of polymers: polyethylene terephthalate (PET), high-density polyethylene (HDPE), polypropylene (PP) and polyvinyl chloride (PVC). An important characteristic of these polymers is that they can not be melted and reprocessed without any serious change in their physicochemical properties. For example, PET remains unmelted at PVC processing temperatures while PVC contamination of PET leads to discoloration of the product. This polymer incompatibility affect physical properties resulting in discoloration and degradation. Consequently it was observed a relatively low price for such mixed plastics compared to virgin polymers (Drelich et al., 1998).

Depending on the application of the recycled PET, some amounts of PVC are tolerable. However, these amounts are generally below 25 ppm and depending on the application and equipment can produce processing problems when the concentration is below 5 ppm (Maczko and kobler, 1993). These difficulties make market for recycled plastic more limited by separation efficiency than of plastic waste demand.

The problem of separation of PVC from PET was studied in this paper. The specific gravity of PVC and PET overlap, e. g. the PVC density ranges between 1.32 to 1.57 g/cm^3 and the PET density varies from 1.33 to 1.37 g/cm^3 (Drelich et al., 1998). Thus, these two polymers cannot be separated using gravity separation techniques. However, these two polymers might be separated by flotation. The possibility of this technically attractive (inexpensive and simple) method for separation of PVC from PVC/PET mixtures has been widely studied (Drelich et al., 1998; Shibata, 1996; Pugh et al., 1998; Le Guern et al, 1997 and 2000).

Figure 1 lists the density of some plastics. It is shown in the diagram that some plastics like PVC and PET, with too slight density difference, are difficult or even impossible to be separated.

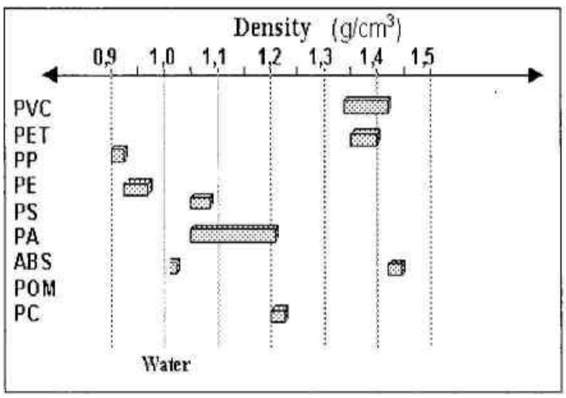

Figure 1: Density of plastics (Pugh et al., 1998). (PVC: polyvinyl chloride; PET: polyethylene terephthalate; PP: polypropylene; PE: polyethylene; PS: polystyrene; PA: polyamid (nylon 6); ABS: acrylonitrile/ butadiene/ styrene; POM: polyoxymethylene; PC: polycarbonate).

Selective flotation separation of the PET/PVC mixture is impossible without changing the surface properties of these polymers. Both polymers exhibit almost the same degree of hydrophobicity. Consequently, it is necessary to render one component of this mixture hydrophilic, while the other component must be maintained in a hydrophobic state, in order to obtain a selective flotation separation. This condition can be achieved by pre-treatment with reagents.

In the present work, two polymers (PVC/PET) were separated from their synthetic mixtures using lignosulphonate as wetting agent. The efficient flotation separation among these two naturally hydrophobic was possible due to selective surfactant adsorption.

EXPERIMENTAL

– Sample preparation

The samples of two different kind of plastics, PVC and PET, were obtained from soft drink bottles. Each of the plastic samples was crushed using a cutting mill and screened. The size fraction used in flotation experiments was -4.00 mm +2.38 mm. The samples used for flotation tests were of different colors (blue PVC and transparent PET) which made it quicker to analyze the concentrate samples through manual sorting at the end of each experiment.

- Reagents

The following reagents were used: sodium and calcium and magnesium lignosulphonate supplied by Clariant, both as depressant; Flotanol supplied by Sigma as frother; calcium chloride ($CaCl_2$) as a source of Ca^{2+} ions; sodium hydroxide (NaOH) and hydrochloric acid (HCl) to adjust pH solution.

– Pre-treatment procedure

The wetting agent used for selective depression was sodium and calcium and magnesium lignosulphonate at concentrations of 50, 100, 300, and 500 mg/L. The plastics samples were treated with those solutions using magnetic stirrer (Fisatom) for 10 minutes before contact angle measurements and flotation tests.

Based on a previous work (Shibata, 1996), the tests were carried out at pH = 6,5. The pH of the solution was adjusted with 0.01 mol/L HCl and 0.01 mol/L NaOH solutions and measured using a laboratory pH-meter (Analion IA 601).

The pre-treatment was necessary after cleaning and before contact angle measurements and microflotation tests. The aim of this conditioning was to promote an adsorption of the reagents on the plastic surface. The adsorption led to a modification of the solid-liquid interface properties.

– Contact angle measurements

The adhering gas bubble method was used in this study; the detailed experimental procedure is the described elsewhere (Florido, P.L., 1999). The contact angle measurements were carried out using a NRL goniometer (Ramé-Hart, Inc.)

The plastic strip (PVC or PET) was placed in the rectangular acrylic chamber. The chamber with the sample was filled with deionized water (or surfactant solution in selected experiments). An air bubble was made at the tip of a U-shaped needle using a microsyringe. The detailed procedure is described elsewhere (Florido, 1999).

- Microflotation tests

The flotation tests were carried out in a 300 mL modified Hallimond tube with 0.5 g of each plastic sample promptly treated. The Flotanol was used as a frother at a concentration of 30 mg/L in all flotation experiments. The suspension of plastics was treated with the conditioning solution for about 10 minutes before flotation experiments. After flotation, the particles (floated and non-floated) were hand sorted. All samples were weighted and flotation recovery was calculated based on the mass balance.

RESULTS AND DISCUSSION

- Contact Angle

The contact angle was measured in order to observe the influence of the lignosulphonate concentration on the hydrophilization of PVC and PET. The effect of sodium and calcium lignosulphonate concentration on the three phase contact angles is presented in Figures 2-5.

Figure 2 shows the effect of sodium lignosulphonate concentration on the contact angle of PVC and PET. It is observed that the PVC contact angle values remains almost constant around 78.6° with a slight fall at a concentration level of 500 mg/L, reaching a value of 55.6°. On the other hand, PET contact angle decreased with the increasing of lignosulphonate concentration, reaching a value around 49.3°.

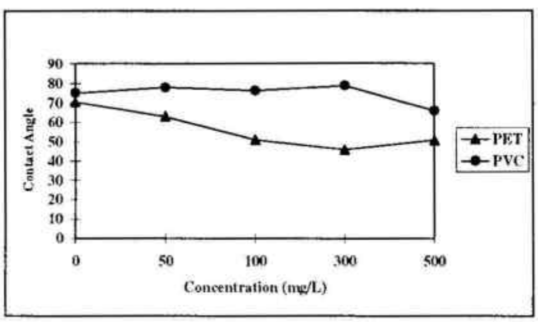

Figure 2: Effect of sodium lignosulphonate concentration on the PET and PVC contact angle measurements at pH 6.5.

Figure 3 shows similar behavior depicted in Figure 2 of the contact angles for PET and PVC with calcium and magnesium lignosulphonate as depressant.

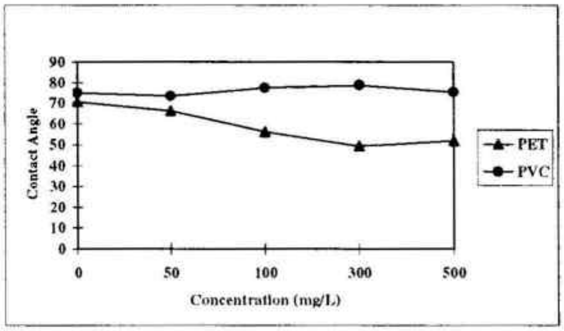

Figure 3: Effect of calcium and magnesium lignosulphonate concentration on the PET and PVC contact angle measurements at pH 6.5.

The contact angles showed in Figures 2 and 3 indicate that a significant difference in hydrophobicity between PVC and PET can be obtained. In order to accomplish selective separation, the greatest difference between contact angle values of PVC and PET was chosen. The best condition of selectivity between PET and PVC is observed at concentration level of 300 mg/L in Figures 2 and 3 where contact angle may be an indicative of selective flotation.

Figure 4 and 5 show that the depressant concentration increasing causes both PET and PVC decreasing of the contact angles values. In Figure 4, it is observed that PET contact angles values presented a significant decrease from 70.5° to 38.3° (at a concentration level of 500 mg/L). The decrease in PVC contact angles was observed to be higher than PET, declining from 50mg/L (42.6°) to 100 mg/L (35.7°) and to 300 mg/L (30.2°).

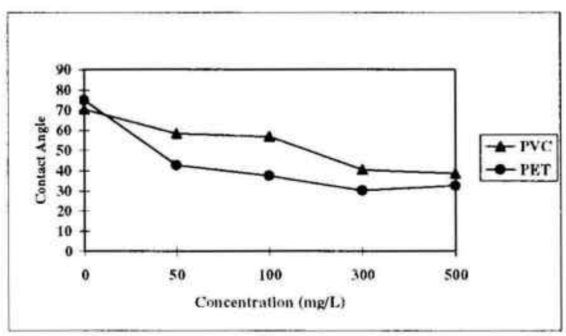

Figure 4: Effect of calcium and magnesium lignosulphonate with Ca^{2+} 10^{-4} mol/L concentration on the PET and PVC contact angle measurements at pH 6.5.

The curves presented in Figure 5 show a significant effect of the concentration of calcium and magnesium lignosulphonate, in the presence of Ca^{2+} 10^{-3}

mol/L, at the hydrophilization for both PET and PVC. PET contact angle values decrease from 70.5° to 29.6° while PVC decreases from 70.0° to 23.5°. As no significant difference in hydrophobicity was observed, it can be considered that no selectivity can be achieved to separate those plastics by flotation, (if Ca^{2+} is present), which is in accordance with the literature (Drelich et al., 1998).

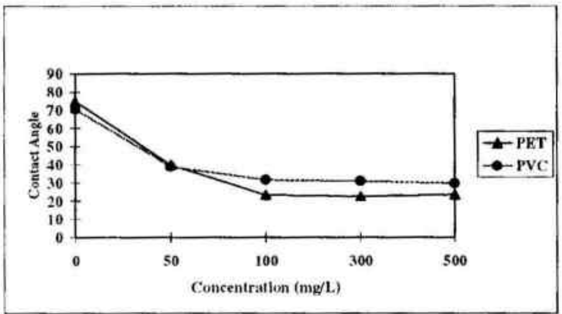

Figure 5: Effect of calcium and magnesium lignosulphonate with Ca^{2+} 10^{-3} mol/L concentration on the PET and PVC contact angle measurements at pH 6.5.

It is interesting to note that the decreasing of the contact angle seems to be caused by was due to the adsorption of depressant; it is important to realize that the presence of Ca^{2+} ions improves the hydrophilization of both PET and PVC.

Similar works have been done on plastics separation (Fraunholcz and Dalmijn, 1997; Stuckrad et al., 1997; Le Guern et al., 2000) by flotation. These results show that the presence of calcium ions play an important role on the decreasing of the contact angle of PET and PVC. Those authors also suggested that the predominant mechanism of adsorption of lignosulphonate may be due to electrostatic and hydrophobic interactions.

- *Microflotation*

Flotation experiments were carried out in order to investigate the effect of the depressant and the presence of Ca^{2+} ion concentration on the flotability of PET and PVC particles.

Figures 6 to 9 present the effect of depressor concentration on the flotation recovery (%). Figure 6 depicts that the increase of sodium lignosulphonate concentration caused a slight depression of PET, from 57.7% to 43.7%, while PVC recovery remained almost constant.

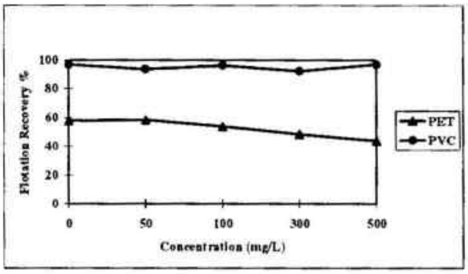

Figure 6: Effect of sodium lignosulphonate concentration on flotation recovery (%) at pH 6.5.

Figure 7 show the effect of calcium lignosulphonate concentration on the flotability of PET and PVC. It can be seen that PET recovery decrease from 57.7% to 25.2% at 500 mg/L of calcium and magnesium lignosulphonate. For PVC, the results are similar to Figure 6.

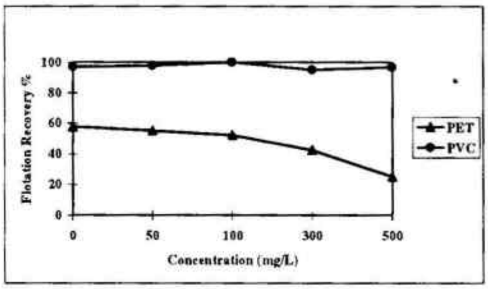

Figure 7: Effect of calcium and magnesium lignosulphonate concentration on flotation recovery (%) at pH 6.5.

Figures 8 and 9 show the flotability of PET and PVC as a function of calcium lignosulphonate in the presence of Ca^{2+} ions. It is observed that PET is significantly depressed, reaching a value of 8.7% recovery (Figure 8) and 2.7% of recovery (Figure 9) at 500 mg/L. In Figure 8, PVC recovery is not affected by the presence of Ca^{2+} (10^{-4} mol/L). But, in Figure 9, in the presence of Ca^{2+} 10^{-3} mol/L, PVC recovery shows a slight decrease.

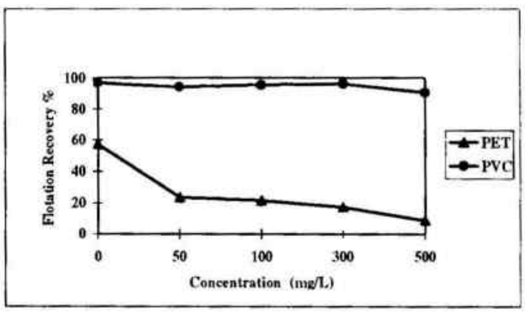

Figure 8: Effect of calcium and magnesium lignosulphonate with ion calcium 10^{-4} mol/L concentration on flotation recovery (%) at pH 6.5.

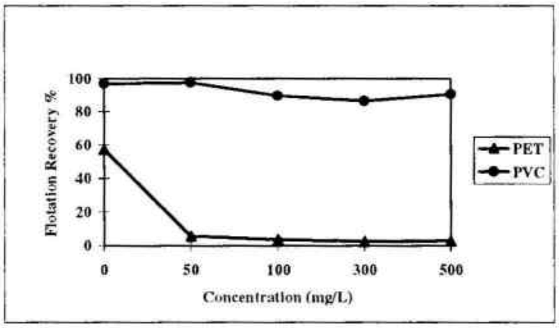

Figure 9: Effect of concentration of calcium and magnesium lignosulphonate with ion calcium 10^{-3} mol/L on flotation recovery (%) at pH 6.5.

Comparing Figures 8 and 9, it can be seen that PET depression improved significantly as the concentration of Ca^{2+} ions increase from 10^{-4} to 10^{-3} mol/L. Figures 8 and 9 show that calcium plays an important role on the depressant action of the lignosulphonate on PET. These tests emphasize that bivalent cations play an important role and have a stronger influence than monovalent ones on the depressant action of lignosulphonate. The results are in accordance with literature (Le Guern et al., 2000; Fraunholcz and Dalmijn, 1997; Tenório and Marques, 2000) which points out the important role of bivalent cations, particularly Ca^{2+} ions, on the selective flotation between PET and PVC. The main interactions involved in lignosulphonate adsorption on the plastics are electrostatic. Calcium plays a role of a bridge between the lignosulphonate molecules and the plastic surface. Calcium can share its two positive charges between the lignosulphonate and the plastics, which was negatively charged. This fact may be justifying the greater recovery when adding Ca^{2+} ions at the lignosulphonate solution.

CONCLUSION

It was possible to separate PVC from PET through flotation using calcium lignosulphonate as a depressant of PET.

Based on the results obtained through contact angle measurements, the best condition of selectivity between PET and PVC was observed using calcium lignosulphonate at a concentration level of 300 mg/L, presenting 78.6° for PVC and 49.32° for PET.

The best flotation results showed that 90.6% for PET recovery can be obtained while rejecting almost all PVC (97.3%) using calcium lignosulphonate as depressant at a concentration level of 500 mg/L in the presence of Ca^{+2} 10^{-3} mol/L. The results showed that bivalent cations such as calcium could play a significant role in the depressant/hydrophilization action of lignosulphonate on PET.

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