Purification of polyethylene terephthalate from polyvinyl chloride by froth flotation for the plastics (soft-drink bottle) recycling industry

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Abstract

Strong alkaline solutions of sodium hydroxide are able to destroy the hydrophobicity of polyethylene terephthalate (PET) allowing for the flotation separation of PVC (polyvinyl chloride) from PET. Conditioning of the PVC/PET mixture in a low-concentration solution of polymer plasticizer at elevated temperature enhances the hydrophobicity of PVC particles and only slightly affects the surface properties of PET particles. On this basis, enhancement of the flotation separation by conditioning with a polymer plasticizer, and by the use of non-ionic surfactants, has been developed and tested at a laboratory scale. Using this procedure a 93–95% recovery of PET can be obtained while rejecting almost all PVC (98–100%). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Plastics recycling offers the potential to reduce fossil fuel consumption because recycled plastics can displace virgin polymers produced from refined fossil fuels. In addition, the energy required to yield recycled plastics may be less than that consumed in the production of polymers from fossil fuels [1].

The problems facing the plastics recycling industry are many but are primarily in the areas of separation and purification. The variety of different plastic materials (often used in one product) is one of the most significant problems in polymer recycling. For example, soft-drink bottles may be clear or colored and are made up of at least five different materials [2]: a polyethylene terephthalate (PET) body (68.7 wt%), a high-density polyethylene (HDPE) base cup (24.4 wt%), a polypropylene (PP) cap (3.6 wt%) or metal cap, a PP label
(2.4 wt%) or paper label, an ethylene–vinylacetate (EVA) copolymer as an adhesive for the base cup and label (0.6–0.7 wt%), and a butadiene/styrene block copolymer gasket in the cap (0.2 wt%). This scenario is further complicated by the fact that the collected soft-drink bottles are always contaminated with bottles made of other polymer(s). For example, edible oil, detergent, and shampoo bottles made of polyvinyl chloride (PVC) frequently enter the process stream for soft-drink bottles.

Most current strategies to separate plastics rely on gravity separation or hand-sorting. Manual separation is labor intensive and expensive. High quality automatic segregation of plastics is not yet reliable. Several commercially viable separations of granulated plastic waste are almost exclusively limited to processes that separate polymers of different specific gravity [3,4]. However, separation of granulated PVC from PET, or classification of the olefin component of the waste stream, cannot be accomplished with such gravity separation technology [3].

A number of promising technologies for the separation of mixed thermoplastics are under investigation and include air classification, hydrocycloning, flotation/sedimentation, depolymerization/purification/repolymerization, selective dissolution, sorting based on infrared analysis or laser scanning of polymers, and incorporation of chemical markers into different polymers [1,5,6]. Up to now, only gravity separation and skin flotation techniques have been used on the industrial scale [7–11]. Froth flotation is also an attractive technique for the plastics recycling industry as shown by the increase in research activities in this area [10–17]. Further, selective dissolution and depolymerization processes have been successfully demonstrated on the laboratory scale for separating plastics based on chemical properties [3,5]. However, selective dissolution requires volatile, often toxic, organic solvents (i.e. xylene, cyclohexane) and it appears to be somewhat expensive.

Further, it is believed that the sorting of mixed plastics might be carried out with a device able to detect some property of the polymer. The property can be a bar code, a spectrographic indicator, NMR signal, etc. [18]. While there is continuing research to facilitate the design of such devices, it is still uncertain whether such automatic separation will be reliable and acceptable to resin suppliers.

The lack of ability to separate a complex mixture of plastics limits the recycling and reuse of most polymers. At the present time, the plastics recycling industry requires relatively pure feed materials as accomplished by expensive hand-sorted classification of waste material. The market for the products of selected polymers such as PET and HDPE is large but only certain polymer streams can be recycled into products that can compete with virgin polymer. In this regard, economical recycling of valuable polymers requires that advances be made in the technologies for separation and recovery of mixed plastics. Selective plastics recycling is an important research area, the development of which will contribute to conservation of limited natural resources.

It was demonstrated in our previous contribution that two polymers, PVC (polyvinyl chloride) and PET, both having the same density and hydrophobic properties, can be selectively separated using the froth flotation technique [17]. This was accomplished by a two-step technology involving alkaline treatment and flotation. During the conditioning of the PVC/PET mixture in a strong alkaline solution, PET is rendered hydrophilic whereas PVC remains in the hydrophobic state [17]. After such a pretreatment step, the selective flotation separation was demonstrated with 95–100% recovery of PET and PVC particles from PVC/PET mixtures of varying composition. However, for some reason similar results could not be obtained with the PET waste contaminated with PVC pine oil bottles. Similarly such an unusual phenomenon is experienced in the ‘real’ recycling industry. In a particular instance a local recycler using a skin flotation approach was unable to separate PVC/PET for European washed bottles. In this study an enhanced technological approach is demonstrated in which the technology presented in our first contribution is extended to the additional step of conditioning the PVC/PET suspension with polymer plasticizers. This step allows us to restore the hydrophobicity of the PVC surface as PVC is easily plasticized. After such a treatment, again high recoveries of PET and PVC are demonstrated using froth flotation.
2. Experimental

2.1. Polymer samples

Samples of virgin shredded polyethylene terephthalate (PET) were received from Recovery Processes International, Inc. (RPI), a plastics recycling technology development company, located in Salt Lake City, UT. The PET originated from newly manufactured PET beverage bottles shredded to 1/2 in size in a plastic granulator.

A few PVC bottles containing pine oil were purchased from the local grocery supply. The empty bottles (after the pine oil was removed) were washed with non-ionic detergent to remove paper labels and residual pine oil. These were rinsed with water several times and dried. The PVC bottles were then cut with scissors to a particle size comparable with PET. The cut pieces were mixed with PET flakes in an appropriate ratio supplying the feed material for experiments.

Contact angle measurements were also performed on larger flat plastic strips cut from the bottles.

2.2. Plastics treatment with alkaline solution

The admixture of plastics was conditioned in alkaline solutions using a Denver agitation machine. The machine was equipped with a two-opposing-flow, three-blade (2.5 in diameter, 45°) marine propeller (800 rpm). The treatment was done in a 21 glass beaker using 300–500 g of the plastics admixture at a solid concentration of 35–45 wt%. The beaker was placed on a hot plate and a constant elevated temperature maintained. Analytical grade sodium hydroxide, NaOH (Mallinckrodt), and tap water were used in these experiments to prepare the alkaline solutions. The admixture of plastics was mixed with the alkaline solution at a temperature of 70–85°C for given periods of time. The sample was screened and rinsed in a stream of tap water after alkaline treatment to remove the treatment solution.

In selected experiments with samples used for contact angle measurements, the polymer strips were conditioned in the alkaline solution using a laboratory magnetic stirrer equipped with a hot plate. Analytical grade NaOH and deionized water were used to prepare the alkaline solutions in these experiments.

2.3. Plastics conditioning with plasticizer

The conditioning of plastics with the plasticizer solution was done in the same agitator which was used for the alkaline treatment, i.e., using a Denver agitation machine. The conditioning was done in a 21 glass beaker using 300–500 g of plastics at a solid concentration of 35–45 wt%. The beaker was placed on the hot plate in order to adjust and maintain the desired temperature. Technical grade plasticizer was used to prepare a 5–40 mg/l solution in tap water. The following plasticizers were used: diisodecyl phthalate (received from Recovery Processes International, Inc., Salt Lake City, UT), diisodecyl azelate, diethylene glycol dibenzoate, and epoxidized linseed oil (Scientific Polymer Products, Inc., Ontario, NY).

Samples of plastics (after appropriate alkaline treatment and rinsing) were mixed with the plasticizer solution for 30–60 min at a temperature of 70–80°C. The suspension of plastics in the plasticizer solution was transferred to a flotation cell after the conditioning operation.

2.4. Flotation experiments

The flotation experiments were conducted in a 21 Denver flotation cell at a rotational speed of about 1300 rpm. The 150–250 g of the plastic sample (promptly treated with the alkaline solution, rinsed, and conditioned with the plasticizer solution) was mixed with 1.81 of tap water. Rhodasurf 91-6 surfactant (C9–11 ethoxylated alcohols) received from Rhone-Poulenc was used as a frother at a concentration of 15–30 mg/l, in all flotation experiments. The pH of the solution was measured with a pH meter. In selected experiments the pH of the solution was adjusted to a desired level using 1–5 M NaOH solutions. The suspension of plastics was conditioned with the frother for about 2 min before the flotation experiments. The froth floated PVC product was collected over 8 min, screened, rinsed with water, and dried. The PET product remaining in the flotation
cell after the experiment was later screened, rinsed and dried.

Following sample drying, the PVC and PET particles were separated from each other by hand-sorting. This was possible due to a difference in color and shape of PVC and PET particles.

All samples were weighed and flotation recovery was calculated based on the mass balance.

2.5. Contact angle measurements

The sessile-drop contact angle measurement technique was used in this study as described in detail in a previous paper [19]. The contact angle measurements were carried out using an NRL goniometer (Ramé-Hart, Inc.).

The treated plastic strip (PVC or PET) was placed on the table of a Ramé-Hart goniometer. A drop of deionized water (pH 5.8–6.2) was placed on the surface of the PVC or PET strip using a microsyringe. The drop size was made to increase or decrease by adding or withdrawing a small volume of water, and the water advancing and receding contact angles, respectively, were measured within 30–60 s. The contact angle measurements for the particular system were done for five to eight large drops having a drop base diameter from 8 to 10 mm. The average values are reported.

3. Results and discussion

It was found in our previous studies [17] that strong alkaline solutions of sodium hydroxide are able to destroy the hydrophobicity (floatability) of polyethylene terephthalate (PET) whereas the hydrophobicity of polyvinyl chloride (PVC) remains only slightly affected by these solutions. On this basis, a technology involving treatment of PET and PVC particles with alkaline solutions followed by froth flotation of PVC with non-ionic surfactants has been developed and tested at a laboratory scale. It was demonstrated that using this technology, a 95–99% recovery of PET can be achieved with the removal of most PVC from the PET [17]. As demonstrated in our previous contribution [17], appropriate NaOH concentration, temperature and time of treatment are required to achieve a significant difference in hydrophobicity between PVC and PET particles. For a variety of PVC/PET samples tested in our laboratory, the 15–30 min of alkaline treatment using 2 wt% NaOH solution at 70–80°C allowed for selective flotation separation of PVC from PET particles [17]. Unfortunately, as observed in our laboratory, such ‘optimum’ alkaline solutions sometimes become too aggressive for the PVC from certain waste streams. Fig. 1 shows the results of contact angle measurements for water drops placed on the surface of the PET and the PVC recovered from a pine oil bottle; both samples were treated with a 2 wt% NaOH solution at about 80°C. It can be seen that both advancing and receding contact angles decreased for alkaline treated plastic surfaces. This effect is more distinct for the PET sample as is quite clear for advancing contact angles. On the other hand, the receding contact angles were reduced down to a few degrees for both polymers after 30 min of alkaline treatment. The receding contact angle results suggest that it will be difficult to separate these particular samples by the initial design of the flotation procedure. Possible reasons for the different behavior of the PVC (from pine oil bottles) in the alkaline solution than from other sources are yet unknown. We suspect that the characteristics of the PVC
surface during alkaline treatment can be affected by the following factors: (i) saponification of residual pine oil adsorbed on the PVC surface; and (ii) destruction of the hydrophobicity and smoothness of the PVC, which may have a different degree of polymerization and be composed of different additives (these issues were not examined in this research).

Fig. 2 shows an example of the flotation results for the PVC particles recovered from pine oil bottles; the same plastic as used in contact angle measurements. A poor flotation recovery (10–15% in 8 min flotation) of the PVC particles, which were treated for 30 min with 2 wt% NaOH solution before flotation, characterized the experiments involving the PVC recovered from pine oil bottles. In comparison, over 90% recovery was obtained for a PVC/PET mixture with ordinary PVC particles treated in an alkaline solution.

Commercial use of a PVC/PET separation process must be capable of removing all PVC from PET down to less than 10 ppm PVC. When such a situation occurs during commercial processing of PVC/PET mixtures, two solutions are possible. First, it appears to be desirable to reduce the conditioning time of alkaline treatment. This, however, might affect the selectivity of the flotation process leading to a significant loss of PET particles with the PVC froth product. The second solution would be to stimulate the restoration/enhancement of the hydrophobicity at the PVC surface. This could be done with plasticizer chemicals. Obviously, the solution chemistry must be controlled in such a way that at the same time the surface of the PET particles remains hydrophilic. This is not an easy task because the literature on the adsorption/absorption of plasticizers at the surface of most polymers ‘practically’ does not exist. On the other hand, over the last several years, Recovery Processes International, Inc. (RPI) has demonstrated that the use of plasticizers improves the hydrophobic properties of PVC surfaces [11]. The diisodecyl phthalate plasticizer, as a surface-modifying agent for the PVC, was also tested in this study and results of contact angle measurements are shown in Fig. 3. The receding contact angle, as measured for the water drop, decreased systematically for the PVC and PET samples treated with the hot alkaline solution (Fig. 3). After 30 min of alkaline treatment, both the PVC and PET samples were conditioned in a hot 5–40 mg/l solution of plasticizer for about

![Fig. 2](image1.png)  
**Fig. 2.** The flotation kinetics of the PVC particles from the plastics waste sample composed of: (1) 1.6 wt% PVC/98.4 wt% PET mixture from the plastics (soft-drink bottle) recycling plant; and (2) 9.2 wt% PVC recovered from pine oil bottles and 90.8 wt% PET recovered from virgin soft-drink bottles. The samples were treated for 30 min with a 2 wt% NaOH solution (75–80°C) and washed before flotation. The flotation experiments were performed in a 2.1 Denver flotation cell (1450 rpm) at 20°C using a 15–20 mg/l Rhodasurf 91-6 surfactant solution (pH 8.0–8.3). The concentration of solids in the flotation cell was about 10 wt%.

![Fig. 3](image2.png)  
**Fig. 3.** Receding contact angles measured with a sessile-drop technique for water drops (8–10 mm base diameter; pH 6) on the PET (detergent bottle) and PVC (pine oil bottle) treated with a 2 wt% NaOH solution at 75–80°C as a function of alkaline treatment time. After 30 min of alkaline treatment the samples were conditioned in a 5–40 mg/l solution (75–80°C) of diisodecyl phthalate plasticizer for 30 min. Samples were rinsed and dried before contact angle measurements.
30 min, rinsed and dried, and receding contact angles were measured again. It was found that the receding contact angle for water on the PET surface practically remained the same whereas it increased from 15–18 to 24–28° for water at the PVC surface (Fig. 3). Evidently, the plasticizer selected for this study "absorbed" preferentially at the PVC surface rather than at the PET surface. However, in some of our experiments it was observed that hydrophobicity of the PET was affected by plasticizer solutions (results not shown here), particularly in solutions of higher plasticizer concentration, indicating that adsorption/deposition of the plasticizer at the surface of the PET can also occur.

Fig. 4 shows the flotation results for the PVC/PET mixtures treated with the alkaline solution and next conditioned with the plasticizer solution. It is clear from Fig. 4 that the temperature of the solution during conditioning is an important parameter. Flotation of the PVC is facilitated at elevated temperatures. The results of flotation at 20°C are practically the same as observed for the PVC/PET mixture treated only with the alkaline solution. Although no fundamental study of plasticizer adsorption was conducted here, it appears to us that the flotation results correlate with the adsorption of diisodecyl phthalate molecules or deposition of plasticizer droplets at the surface of polymer(s). It seems that the adsorption/deposition of the diisodecyl phthalate at the PVC surface is enhanced at an elevated temperature.

The effect of the solution pH in flotation is shown in Fig. 5. The flotation recovery of PVC decreased with increasing alkalinity. Of course the negative charge at the polymer–water and water–air interfaces are expected to increase in alkaline solutions. Also, the effect of pH on the kinetics and the extent of plasticizer adsorption/deposition at these interfaces could be a significant factor. These issues, however, require additional research before reaching a complete description of the chemical phenomena occurring at the polymer–water and water–air interfaces.

Diisodecyl phthalate is not the only plasticizer which can be used for relatively 'selective' restoration of hydrophobicity at the PVC surface after alkaline treatment. Several other plasticizers were tested in this study and the separation results of the most promising chemicals are shown in Fig. 6. All three plasticizers (diisodecyl azelate, diethylene glycol dibenzoate, and epoxidized linseed oil)
demonstrated applicability for PVC separation from the PVC/PET mixtures. However, as shown in Fig. 6, each plasticizer had a slightly different effect on the kinetics of flotation.

Fig. 7 presents examples of PET recovery obtained in the flotation experiments involving PVC/PET mixtures. The results are representative of most of the experiments conducted in this study. First, it was found that an increase in flotation temperature had a positive effect on the selectivity of the flotation separation. Second, the recovery of PET particles during 8 min of flotation was usually between 93 and 95 wt% at a flotation temperature above 50°C.

4. Proposed technology

The results of this study indicate that the selective recovery of PET from the PVC/PET mixtures cannot always be accomplished in a two-step process involving alkaline treatment and froth flotation. Hydrophobicity of the PVC from certain bottle products, such as pine oil bottles used in this study, may sometimes be reduced, or even destroyed, by alkaline solutions and no selectivity in the PVC flotation can be achieved for the PVC/PET mixtures. These results explain the anomalous results obtained by RPI when attempting to process varied PET/PVC mixtures. In particular, ‘soy’ PVC from Japan and ‘olive oil’ PVC from Israel.

For such mixtures, an additional step in this technology leading to a restoration of the PVC hydrophobicity is proposed. A simplified flowsheet for the proposed technology is shown in Fig. 8. Preliminary steps include the particle size reduction and sizing of the plastic waste. The size of the PVC and PET particles should not be greater than about 10 mm for the froth flotation step.

The plastic particles of appropriate size are treated with the alkaline solution (Fig. 8). The results from our previous research [17] indicate that this step should be accomplished with hot alkaline solutions (70–80°C, 1–3 wt% NaOH, 15–30 min) in order to destroy the hydrophobicity of the PET. Unfortunately, the hydrophobicity of the PVC originating from certain PVC bottles might also be reduced to a low level during alkaline treatment. The hydrophobicity of the PVC can be at least partially restored during conditioning of
this plastic with selected polymer plasticizer(s) at an elevated temperature. The research in this project indicates that such plasticizers as diisodecyl phthalate, diisodecyl azelate, diethylene glycol dibenzoate, and epoxidized linseed oil have an affinity to the PVC and much reduced affinity to the PET. In this regard, these plasticizers can be used in the froth flotation technology proposed in this study for removal of PVC and purification of the PET.

Plastics should be screened and rinsed with water before conditioning with the plasticizer solution. The results from our laboratory (not shown here) indicate that restoration of the PVC hydrophobicity should not be done in highly alkaline solutions due to saponification side reactions.

The froth flotation separation follows alkaline treatment and plasticizer conditioning in the plastic processing technology as shown in Fig. 8. The results from our research indicate that the flotation efficiency is reduced for alkaline suspensions and thus, the pH value of the suspension needs to be adjusted from pH 6 to 9. The concentration of particles in the suspension should remain at a level of 7–15 wt%. The frother used in this study is the non-ionic surfactant (Rhodasurf 91-6: C9–11 ethoxylated alcohols) at a concentration of 15–30 mg/l. However, other frothers with strong frothing abilities and lack of affinity for the PVC and PET polymers can also be used.

5. Conclusions

The research program was designed to improve and broaden the flotation technology for the removal of PVC from PVC/PET mixtures. The PVC and PET polymers with unmodified surfaces exhibit similar hydrophobicity and thus selective flotation of the PVC from the untreated PVC/PET mixtures is not possible. 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 chemical treatment involving a strong alkaline solution and low-concentration solution of appropriately selected poly-
mer plasticizer. The selective flotation process would involve a three-step sequence: (1) treatment of plastics with strong alkaline solutions; (2) conditioning of plastics with a solution of plasticizer at an elevated temperature; and (3) flotation separation at an elevated temperature in the presence of frother. Using this technology for samples from selected sources, a recovery of 93–95 wt% PET was obtained.

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