Iranian Polymer Journal
19 (7), 2010, 483-489

Available online at: http://journal.ippi.ac.ir

Selective Separation of PVC from PET/PVC Mixture Using Floatation by Tannic Acid Depressant

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Received 17 May 2009; accepted 25 May 2010

ABSTRACT

Production and consumption of plastic materials have increased in recent decades. The increase in plastic production and consumption has been largely responsible for the increase in plastics waste production. The problem of plastics waste is quite important in terms of environmental sustainability and solid waste management. Plastics recycling requires the separation of materials insofar as being almost pure. To achieve this goal in an economical way, technologies developed in mineral processing are of great help. Each method has certain capabilities and limitations. Instance separation of PET and PVC by gravity techniques is practically not applicable, due to slight differences in density. In this research, separation of PET and PVC by selective floatation was studied. The use of floatation for plastic separation is particularly challenging because of inherent hydrophobic nature of plastics surfaces. To separate PET and PVC, from the mixture of the two, by floatation should make one of them hydrophilic and wettable by water. This can be achieved by several methods among which the addition of a wetting agent that interacts with the surface layer is one of many techniques designed. In this study, tannic acid was employed as the depressant of PET. The results showed that, virgin materials can be separated with 99.62% efficiency. In the case of post-consumer PET and PVC, 88.40% separation efficiency was achieved at optimum conditions. Also, in virgin and postconsumer materials, difference in the contact angles of PET and PVC increased as tannic acid dosage increased. Besides, the results indicated that the pH of the conditioning step is vital with respect to separation efficiency.

Key Words:

plastic separation;
polyvinyl chloride;
polyethylene terephthalate;
selective floatation;
contact angle.

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INTRODUCTION

Nowadays, needless to say, plastics play an undeniable role in multitude of worldwide applications. Besides their rather cheap cost, light weight, and longevity, plastics could be synthesized with a wide range of properties. Therefore, the global production of plastics has grown exponentially over recent years and correlates quite well with the population growth [1]. The increments in plastics production and consumption are largely responsible for the increments in solid waste production [2]. Consequently, this growth has led to a global environmental challenge [3].

To dispose plastic waste, several methods have been introduced, namely land filling, energy recovery, reuse and recycling [4]. Plastics disposal in a landfill requires a wide area and the plastics themselves need a very long time to be degraded [5,6]. The methods of waste conversion to energy also generate unacceptable emissions of gases such as nitrous oxide, sulphur oxides, dusts, dioxins and other toxins [7]. Especially, waste plastics containing PVC pollute the environment and shorten the service life of the incinerator as generating hazardous HCl gas, dioxins containing Cl, etc. [4,8]. Furthermore, the emphasis has now been shifted to a more practical application with the attitude that the plastic wastes can be considered as a potential useful energy resource [1]. As a result, the amount of plastics that are being recycled is increasing due to higher landfill costs, legislative pressures and public support for recycling initiatives [9].

Plastics recycling encompasses four activities; namely collection, separation, reprocessing and marketing. Therefore, developing methods and techniques to separate valuable materials from wastes which can be reused or reprocessed to produce new products is necessary. To this end, technologies developed in mineral processing can be of great help [10]. Several separation technologies, like gravity methods, jigging and wet shaking table or their combination [11], electrostatic separation [12], froth floatation [13-15] and sink-float separation [16], can be implemented to separate mixed plastics wastes into its individual components. Each method has certain capabilities and limitations. For instance, in the case of PVC and PET mixed wastes, due to slight differences in their densities (i.e., PET and PVC = 1.30-1.35 g/cm^3) [17,18], gravity separation of these two is practically not possible.

The general approach in separation by floatation is a suitable surface treatment method to obtain selective separation by froth. Thermodynamic analysis of the floatation system indicates that the main parameter of floatation is a combination of contact angle and surface tension [19] (eqn (1)).

$$\Delta G_f = \gamma_{lg}(\cos\theta - 1) \qquad (1)$$

where ΔG_f is Gibbs thermodynamic potential (free enthalpy) (mJ/m^2); γ_{lg} is liquid-gas interfacial tension; and θ is contact angle (in degrees).

It can be seen that floatability of materials increases with the contact angle [20]. Therefore, when plastics have similar density, larger contact angle signifies higher floatability [21,22]. It is reported that using floatation technology is economically feasible for separation of acrylonitrile-butadiene-styrene/high impact polystyrene (ABS/HIPS) from their mixed wastes [23].

In this research work, the separation of PET and PVC from virgin materials and mixed post-consumer plastics wastes in presence of tannic acid as a depressant of PET was investigated by floatation. The separation efficiency with respect to the depressant dosage and pH are also evaluated by contact angle measurement and floatation recovery. In the past, our major works involved the floatation experiments which we carried out by column cell floatation, with the difference that we used conventional floatation cells. These cells have higher capacity and easier scale up and handling. Also, in a more recent attempt [18], PET particles have been separated with 57.0% efficiency and 99.7% purity in post-consumer polymer separation.

EXPERIMENTAL

Materials

Virgin granular and post-consumer PET and PVC have been employed in this study. Virgin PET and PVC were obtained from Shahid Tondgooyan Petrochemical Co. and Mahshahr Petrochemical Co. (Iran), respectively. Post-consumer PET and PVC were collected from shredded products of a local municipal recycling facility. The original shredded PET and PVC were obtained from beverage bottles. Samples of post-consumer plastics were screened into different size fractions. A fraction of -6.23+ 2.78 mm (-3+8 mesh) was used in the experiments.

The wetting agent used for selective depression of PET was tannic acid (TNA) (BDH, England), and methyl isobutyl carbinol (MIBC) was used as the frothing agent (Merck, Germany). 1 M NaOH and 25% HCl solutions were used to adjust pH of the solution to a desired level.

Methods

Plastics Treatment with Tannic Acid Solution

The admixture of plastics was conditioned in tannic acid solution using an agitator at 800 rpm. The treatment was carried out in a 1.5-L glass beaker using 120 g of each plastic sample at a solid concentration about 20 wt%. The pH of the medium was adjusted to the desired level. The admixture of plastics was mixed with a predetermined dosage of tannic acid solution at adjusted temperature for 3 min. The pulp was then dewatered on a screen and rinsed to remove the access reagent.

Floatation Experiments

The floatation experiments were carried out in a 2-L Denver floatation cell at a low rotational speed of about 600 rpm. Each plastic sample of 120 g was promptly treated with the tannic acid solution, rinsed and then repulped with 1.8 L of tap water. MIBC was added as a frother at the concentration of 80 ppm in all experiments. After 30 s conditioning time in the presence of frother, the air valve was opened and the floated product was collected for 2 min. The floated and sunken products were screened, rinsed with tap water and dried at 70°C.

The PVC and PET particles presented in each product were separated from each other manually. This was possible due to difference in the colour of PVC and PET particles.

All subsamples were weighed and their floatation recovery and separation efficiency as given in eqn (2) were calculated. The effectiveness of the floatation tests was determined by calculating the separation efficiency, which combined the recovery and grade data into a single value [19,24]. The separation efficiency is defined as a percentage data:

$$\textit{Separation efficiency } (\%) = (\textit{Float recovery of PVC} - \textit{Float recovery of PET}) \times 100 \qquad (2)$$

All floatation tests were repeated three times and the average is reported here.

Contact Angle Measurements

An angle formed between a water droplet in contact with a solid surface is referred to "contact angle" [25]. For contact angle determination of virgin PET and PVC, the samples were prepared using compression moulding in 2×1 cm dimensions (Toyo Seiki, JP).

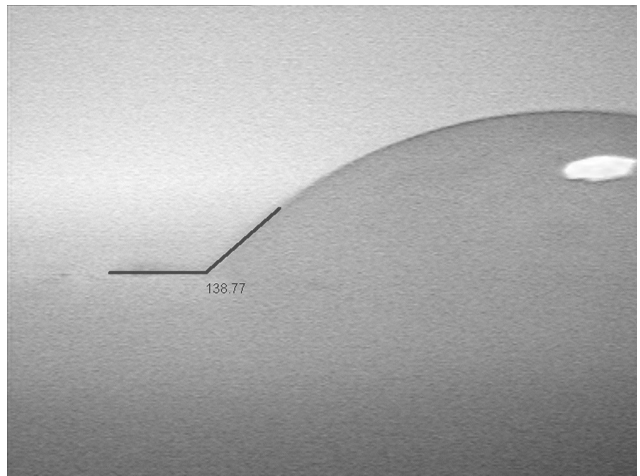


Figure 1. Supplemental measurement of a hydrophilic sample.

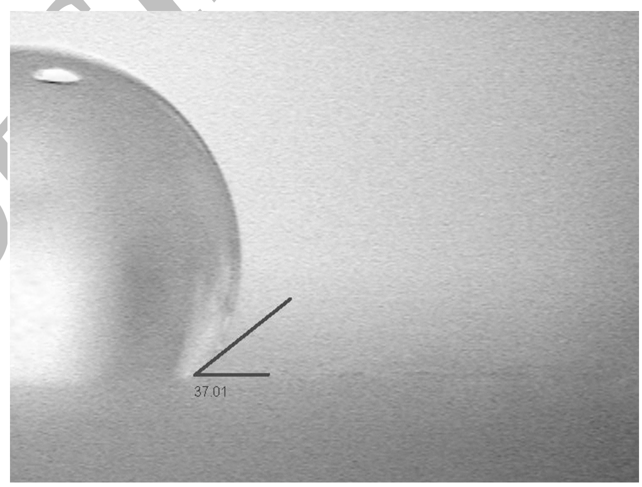
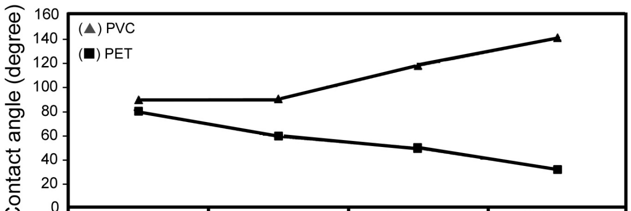


Figure 2. Supplement measurement of a hydrophobic sample.

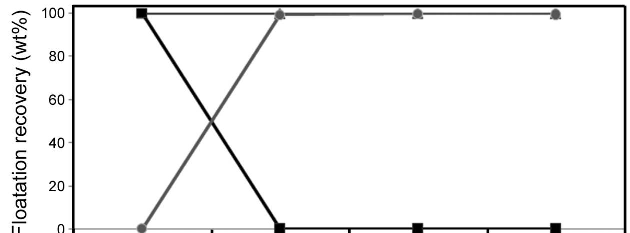
Also, for contact angle determination of consumer material flat plots of consumer materials with 2×1 cm dimensions were utilized. The contact angles were measured by a direct method [1] as shown in Figures 1 and 2. A drop of distilled water was placed on the surface of each sample through a micro-syringe and the image of equilibrium contact angle was taken by a camera with sufficient enlargement. Images were processed by computer and the contact angles were determined by a software tool [26]. This process was repeated eight times for each sample and the average was considered as the contact angle of the sample. Note that in this work, the supplemental specimen was measured and then contact angle was calculated.



	0	0.00004	0.0001	0.0002
(▲) PVC	88.72±(2.83)*	89.56±(9.93)*	116.93±(3.22)	140.02±(7.10)
(■) PET	79.35±(3.21)	58.83±(0.69)	49.33±(8.93)	31.76±(8.88)

*(SD) Tannic acid concentration (M/L)

Figure 3. Variation in contact angles of virgin materials versus tannic acid concentration.



	0.00000	0.00004	0.00010	0.00020
(▲) PVC	99.96±(0.03)*	99.80±(0.21)	99.89±(0.08)	99.69±(0.46)
(■) PET	99.75±(0.07)	0.28±(0.18)	0.27±(0.13)	0.20±(0.10)
(●) SE	0.21	99.22	99.62	99.49

*(SD) Tannic acid concentration (M/L)

Figure 4. Floatation response of virgin PET and PVC as a function of tannic acid concentration at constant pH 7.5.

RESULTS AND DISCUSSION

Virgin Plastics

Effect of Tannic Acid Concentration on Contact Angle

The variations of contact angles of PET and PVC against tannic acid concentration are given in Figure 3. As shown in this figure, the contact angle of PET decreases with increased tannic acid concentration from 0.00 to 2×10^{-4} M/L. Meanwhile, the contact angle of PVC increases with increased tannic acid concentration of the same range. Therefore, by increasing the tannic acid concentration, while PVC became more hydrophobic the PET became more hydrophilic. Consequently, as it was expected the selectivity in floatation separation of PET/PVC improved by increasing of tannic acid concentration.

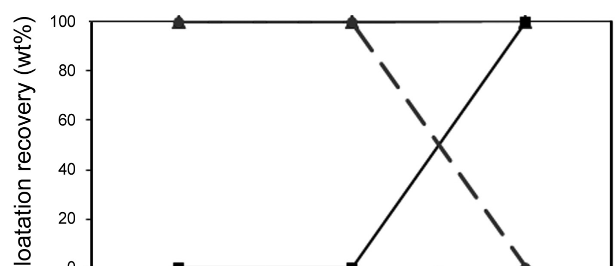
Effect of Tannic Acid Concentration on Floatability

The effect of tannic acid concentration on the recovery of PET and PVC in the floated product at pH 7.5 and constant temperature (25°C) is shown in Figure 4. The results indicate that addition of tannic acid with dosage of 5×10^{-5} to 2×10^{-4} M/L in treatment phase; had no significant effect on PVC floatability, although the PET floatability decreased sharply. Also change of tannic acid concentration within the same range had no notable depressant effect on PET particles. The maximum difference in the recovery of PVC and PET plastics in the floated product is obtained by adding 1×10^{-4} M/L tannic acid in the treatment phase. Therefore, floatation experiments with tannic acid produced high recovery and pure products.

Tannic acid is a macromolecular depressant and contains many hydrophilic groups (mainly -OH). When tannic acid is adsorbed selectively on PET by physisorption, the PET particles acquire hydrophilic role, whereas tannic acid is less adsorbed on PVC and its particles remain hydrophobic.

Effect of pH on Floatability

Figure 5 shows the effect of pH solution on the recovery of PET and PVC in the floated product at fixed tannic acid concentration (1×10^{-4} M/L) and temperature (25°C). As it is observed in Figure 5, the recovery of floated PET increases dramatically when pH changes from acidic to basic condition. This situation can be explained because of tannic acid structure. The phenolic OH-groups contained in its structure possess a weak acidic nature, therefore, tannic acid dissociates noticeably at basic values of



	5.5	7.5	9.5
(▲) PVC	99.82±(0.21)	99.86±(0.08)	99.93±(0.24)
(■) PET	0.14±(0.18)	0.40±(0.27)	99.87±(0.24)
(●) SE	99.68	99.46	0.06

pH

Figure 5. Floatation response of virgin PET and PVC as a function of pH in presence of 1×10^{-4} M/L tannic acid.

Table 1. Floatation results at optimum conditions for virgin PET and PVC separation.

Product	Weight (%)	Content (%)		Recovery ± SD (wt%)	
		PVC	PET	PVC	PET
Floated	50.10	99.73	0.27	99.89 ± 0.08	0.27 ± 0.11
Sunken	49.90	0.11	99.89	0.11 ± 0.08	99.73 ± 0.11
Feed	100.00	50.00	50.00	100	100

pH [27]. The results exhibit that pH changing from 5.5 to 9.5 had no significant effect on the PVC recovery, but by pH varying from 7.5 to 9.5 the recovery of PET in floated product increased from 0.40 wt% to 99.87 wt%. It can be said that PET/PVC selective separation in the presence of tannic acid declined in the basic condition. In other words, tannic acid loses its depressant effect in alkaline region. The similar results have been reported elsewhere [1,27].

Results of Floatation Experiment under Optimum Conditions

According to the previous experiments, optimum conditions for virgin PET and PVC separation were determined as: tannic acid concentration of 1×10^{-4} M/L and pH 7.5. At the end of the floatation experiments, PVC particles were separated from PET particles at 99.73% purity and 99.89% recovery, with separation efficiency of 99.62%. The results obtained with optimized conditions are illustrated in Table 1.

Post-consumer Plastics

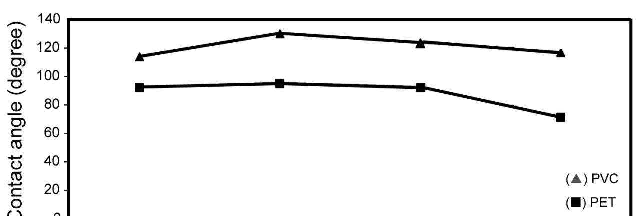
Effect of Tannic Acid Concentration on Contact Angle

The contact angles of post-consumer PET and PVC were measured in different tannic acid concentrations from 0.00 to 3×10^{-5} M/L. The obtained results are shown in Figure 6. The obtained results show that the difference of PET and PVC contact angles increases with increasing tannic acid concentration. Therefore, the selectivity of separation improves with increased tannic acid concentration. Also Figure 6 indicates that contact angles of untreated post-consumer PET and PVC are higher than contact angles of untreated virgin PET and PVC.

Effect of Tannic Acid Concentration on Floatability

Figure 7 shows the floatation tests result according to tannic acid concentration. Experiments were conducted at pH 7.5, constant temperature (25°C) and the concentration of tannic acid was changed from zero to 3×10^{-5} M/L. As it is observed in Figure 7, the recovery of floated PET in the presence of tannic acid sharply drops to under 6%, while the recovery of floated PVC drops only slightly to about 90%.

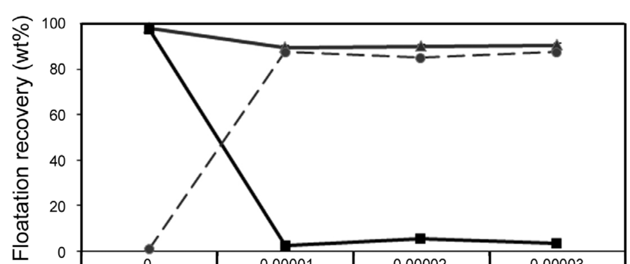
Also best separation efficiency was 87.49%, obtained at 3×10^{-5} M/L tannic acid concentration.



	0	0.00001	0.00002	0.00003
(▲) PVC	113.71±(3.24)	129.89±(9.47)	123.6±(13.97)	116.85±(16.38)
(■) PET	92.74±(8.38)	95.23±(3.75)	92.56±(3.95)	71.96±(6.71)

Tannic acid concentration (M/L)

Figure 6. Variation in contact angles of post-consumer materials versus tannic acid concentration.



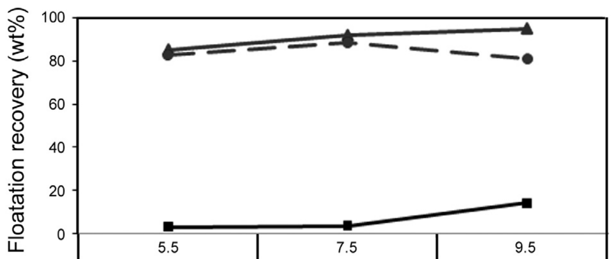
	0	0.00001	0.00002	0.00003
(▲) PVC	98.21±(1.35)	89.56±(3.14)	90.10±(1.86)	90.70±(4.05)
(■) PET	97.63±(1.83)	2.22±(1.11)	5.37±(3.73)	3.21±(0.28)
(●) SE	0.58	87.34	84.73	87.49

Tannic acid concentration (M/L)

Figure 7. Floatation response of post-consumer PET and PVC as a function of tannic acid concentration at constant pH 7.5.

Table 2. Floatation results at optimum conditions for post-consumer PET and PVC separation.

Product	Weight (%)	Content (%)		Recovery ± SD (wt%)	
		PVC	PET	PVC	PET
Floated	47.69	96.34	3.66	91.89 ± 1.86	3.49 ± 0.56
Sunken	52.31	7.75	92.25	8.11 ± 1.86	96.51 ± 0.56
Feed	100.00	50.00	50.00	100	100



	5.5	7.5	9.5
(▲) PVC	85.26±(2.69)	91.89±(1.53)	94.96±(3.49)
(■) PET	2.93±(1.19)	3.49±(0.49)	14.19±(1.08)
(●) SE	82.33	88.40	80.77

pH

Figure 8. Floatation response of post-consumer PET and PVC as a function of pH in presence of 3×10^{-5} M/L tannic acid.

Effect of pH on Floatability

Figure 8 shows the floatation tests result according to pH solution at constant tannic acid concentration (3×10^{-5} M/L) and temperature (25°C). In Figure 8, it can be observed that when pH increases from 5.5 to 9.5, the recovery of floated PET increases from 2.93% to 14.19%, while the recovery of floated PVC improves from 85.26% to 94.96%. In other words, floated PET and PVC increased with pH increases. Moreover, best separation efficiency was obtained at pH 7.5 with magnitude of 88.40%.

Result of Floatation Experiment at Optimum Conditions

According to the previous experiments, optimum conditions for post-consumer PET and PVC separations were determined as: tannic acid concentration of 3×10^{-5} M/L and pH 7.5. At the end of the floatation experiments, PVC particles were separated from PET particles at 96.34% purity and 91.89% recovery, with separation efficiency of 88.40%. The results obtained at optimized conditions are illustrated in Table 2.

CONCLUSION

The separation of PET and PVC from mixes of the two polymers can be achieved by floatation using tannic acid as a wetting agent for PET, and methyl isobutyl carbinol (MIBC) as frother. The results indicated that the pH of the conditioning step is vital with respect to separation efficiency. Within the increments used in this research work, the optimum pH for separation of PET and PVC was found to be pH 7.5. Therefore, the best separation of virgin material was achieved with 1×10^{-4} M/L tannic acid concentration and pH 7.5. Under these conditions, PVC particles were separated from PET particles to 99.73% purity and 99.89% recovery. Also, the highest separation efficiency of post-consumer plastics was gained with 3×10^{-5} M/L tannic acid concentration and pH 7.5. In floatation experiment at optimized conditions, PVC particles were separated from PET particles to 96.34% purity and 91.89% recovery.

From economical viewpoint, this method for separation of plastics is profitable. Because of the high purity of the recovered products, the quality of consumer products are not affected. Also the energy and disposal cost are saved. Because the plastics are to be recycled rather than placed in a landfill and because no organic solvents are used in the recovery process, the public will certainly enjoy a cleaner environment.

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