

## Effects of additives on PVC plastics surface and the natural flotability



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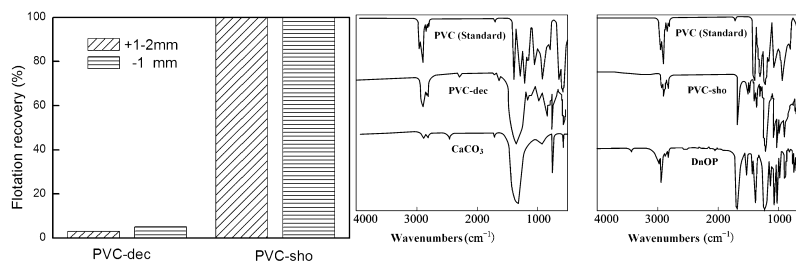
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### HIGHLIGHTS

- The effects of additives on PVC plastics surface are investigated.
- The additives have significant impacts on the surface free energy.
- CaCO<sub>3</sub> improves the hydrophilicity and drops the flotability.
- DnOP enhances the hydrophobicity and increases the flotability.
- Flotation tests were conducted to study the natural flotability of PVC plastics.

### GRAPHICAL ABSTRACT

As shown in the figure, PVC plastics with different additives show significant difference in the flotability. The effects of additives on the PVC plastics surface and the natural flotability are investigated through calculation of surface free energy and interaction free energy and flotation tests.



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### ABSTRACT

The polyvinyl chloride (PVC) plastics with calcium carbonate (CaCO<sub>3</sub>) or di-n-octyl phthalate (DnOP) serving as additive were chosen to investigate the effects of additives on the surface of PVC plastic, and flotation tests were conducted to study the natural flotability of PVC plastics. The surface free energy of the polished and original surface of PVC plastics demonstrates that the crushed or shredded particles in the flotation system present the true surface property of plastics, and the additives show significant impacts on the surface free energy of PVC plastics. The addition of CaCO<sub>3</sub> results in an increase of the attraction force between plastic surface and water, and a decrease of the adhesion force between plastic surface and bubble, and thus the flotability is reduced. DnOP decreases the attraction force between plastic and water and increases the adhesion force between plastic and bubble, and thus the hydrophobicity of plastic is enhanced while the flotability rises. Flotation tests of PVC plastics and waste PVC plastics confirmed the above conclusions, and infrared spectra of the two waste plastics verified the influence of the additives. These conclusions provide some insights into flotation technique with respect to plastic separation, especially for the recovery of waste PVC plastics.

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## 1. Introduction

Plastics have been one of the most widely used materials in our daily life and industrial production [1,2], and the amount of waste plastics increases sharply in recent decades owing to the

mass production, heavy consumption and the short service life of plastics. Moreover, waste plastics lead to a series of problems, such as environmental pollution and waste of resources [3,4]. Recycling allows waste plastics to be reused, reducing its production cost and disposal problem.

Plastics recycling involves primarily four steps, namely collection, separation, reprocessing and marketing [5], and separation is the bottleneck at present. Due to their superior intrinsic flotability, plastics can be separated by flotation. Compared with the alternative methods, such as electrostatic separation [6,7], sink–float

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**Table 1**  
Ingredients of PVC plastics.

Ingredients (wt)	Ca <sub>0</sub>	Ca <sub>10</sub>	Ca <sub>20</sub>	Ca <sub>30</sub>	Ca <sub>40</sub>	Ca <sub>50</sub>	Ca <sub>60</sub>
PVC resin	100	100	100	100	100	100	100
Tribasic lead sulfate	4	4	4	4	4	4	4
Dibasic lead phosphite	2	2	2	2	2	2	2
Lead stearate	1	1	1	1	1	1	1
Barium stearate	1	1	1	1	1	1	1
Paraffin	1	1	1	1	1	1	1
Calcium carbonate	0	12	27	47	73	109	164

Ingredients (wt)	DP <sub>0</sub>	DP <sub>10</sub>	DP <sub>15</sub>	DP <sub>20</sub>	DP <sub>25</sub>	DP <sub>30</sub>	DP <sub>40</sub>
PVC resin	100	100	100	100	100	100	100
Dibutyl phthalate	18	18	18	18	18	18	18
Tribasic lead sulfate	2	2	2	2	2	2	2
Lead stearate	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Barium stearate	1	1	1	1	1	1	1
Paraffin	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DnOP	0	14	22	31	41	53	82

separation [1,8], and hydrocyclone [9], plastics flotation demonstrates some exciting advantages such as superior separation efficiency and cost-effective [10]. Plastics flotation has been the focus of considerable researches [11–13].

Polyvinyl chloride (PVC) is one of the major synthetic resins, and is widely used in the building, packing, and automobile industry. Additives such as calcium carbonate (CaCO<sub>3</sub>) and di-n-octyl phthalate (DnOP) are often added in production of plastics to improve the properties of plastics or lower the cost [14–16]. Based on our previous study, additives have certain impacts on the flotation behavior of waste plastics [17]. From preliminary tests, it was found that there were significant differences in the flotability of PVC plastics in various application areas. The natural flotability is defined as the flotation recovery when flotation tests are conducted without reagents. This paper focuses on the effects of additives on the surface of PVC plastics and further investigates the natural flotability of PVC plastics.

## 2. Materials and methods

### 2.1. Materials

PVC plastics (Table 1) with different content of calcium carbonate (CaCO<sub>3</sub>) or di-n-octyl phthalate (DnOP) serving as additive and waste PVC plastics were chosen to investigate the effects of additives on the surface of PVC plastics. The samples of waste PVC plastics were achieved from decorative buckle and rain boot, and they were referred as PVC-dec and PVC-sho in this paper, respectively. The plastic samples for flotation tests were shredded and screened, and the sieve size used in this study was –1 mm and +1–2 mm.

Distilled water, glycerol, formamide, ethylene glycol and diiodomethane were used as probe liquids to measure the contact angles between the liquids and surface of PVC plastics; glycerol, formamide, ethylene glycol and diiodomethane were chemically pure and used as received. Tap water was used throughout the flotation tests.

### 2.2. Flotation equipment and test procedure

The flotation tests were conducted for about 6 min in a glass column with a height of 170 mm and a diameter of 30 mm. Air was passed through the sand core to produce gas bubbles, and the airflow rate was 6 ml min<sup>-1</sup>. At the end of the flotation test, the overflowed and submerged plastic particles were collected, rinsed with tap water, dried in atmosphere, and weighed.

**Table 2**  
Surface free energy (mJ m<sup>-2</sup>) of various plastic surfaces.

Surfaces	$\gamma_s$	$\gamma_s^{LW}$	$\gamma_s^+$	$\gamma_s^-$
Original surface of PVC resin	48.33	43.41	1.73	3.50
Polished surface of PVC	48.28	43.36	1.73	3.49
Original surface of PVC-Ca <sub>0</sub>	47.39	43.14	1.36	3.32
Polished surface of PVC-Ca <sub>0</sub>	51.39	46.17	0.84	8.11
Original surface of PVC-Ca <sub>50</sub>	47.72	43.22	1.38	3.67
Polished surface of PVC-Ca <sub>50</sub>	52.93	46.83	0.50	18.62
Original surface of PVC-DP <sub>0</sub>	39.51	36.92	0.41	4.10
Polished surface of PVC-DP <sub>0</sub>	44.84	40.66	0.67	6.53
Original surface of PVC-DP <sub>30</sub>	37.68	35.98	0.18	4.01
Polished surface of PVC-DP <sub>30</sub>	40.13	37.01	0.40	6.07

Note.  $\gamma_s$  is the total surface free energy of solid, namely the sum of  $\gamma_s^{LW}$ ,  $\gamma_s^+$  and  $\gamma_s^-$ .

### 2.3. Measurement of contact angle

Before the measurement of contact angle, different kinds of surfaces were prepared to detect the contact angles. Plates of PVC resin and PVC plastics with different content of additives were tailored into 20 mm × 20 mm, and then put into tap water containing washing powder, tap water and distilled water in ultrasonic generator (Shanghai Ultrasonic Co. Ltd., China) for 10 min in sequence to clean, respectively. In order to study the impacts of additives, the polished surface of PVC resin and PVC plastics were prepared. Plates of PVC resin and PVC plastics were cut into 20 mm × 20 mm, lapped by hand using 400-mesh oilstone, polished through 800-mesh and 1200-mesh waterproof abrasive paper, and then washed in the same way demonstrated above.

A JJC-I contact angle measuring instrument (Changchun Optical Instrument Factory, China) is employed to measure the contact angle of liquid on the solid surface, and the measurement of contact angle is demonstrated in detail in our previous paper [13].

### 2.4. Calculation of surface free energy and interaction free energy

The surface free energy of plastics was calculated using the Lifshitz–van der Waals/acid–base approach [18,19]. As shown in Eq. (1), parameters of solid surface energy can be obtained through measuring the contact angle between the solid surface and three liquids [20].

$$(\gamma_L^{LW} + 2\sqrt{\gamma_L^+ \gamma_L^-})(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (1)$$

where  $\theta$  is the contact angle between liquid and solid;  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  are parameters of the surface free energy, namely the Lifshitz–van der Waals (LW) component, Lewis acid component and Lewis base component, respectively. The subscripts L and S denote liquid and solid, respectively.

## 3. Results and discussion

### 3.1. The effects of additives on the surface of PVC plastics

#### 3.1.1. Surfaces of plastic particle in flotation system

Based on the determined data of contact angles, surface free energy of various surface were calculated and the results are shown in Table 2. It is observed that both the original and polished surfaces of PVC resin show similar surface properties, which can be ascribed to the uniformity of PVC resin. The difference in surface free energy between PVC-Ca<sub>0</sub> and PVC resin may be owing to the effects of low-surface-energy substances such as paraffins, while surface free energy of PVC-Ca<sub>50</sub> reflects the impacts of the stabilizers such as lead stearate. The surface free energy of the original surface of PVC-Ca<sub>0</sub> and that of PVC-Ca<sub>50</sub> are similar, but the surface free energy of

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