اثرات مواد افزودنی بر روی سطح پلاستیکهای PVC و قابلیت شناوری ذاتی آنها

چکیدہ

پلاستیکهای پلیوینیلکلراید (PVC) با افزودنیهایی مانند کربنات کلسیم (CaCO3) یا دی-n-اکتیل فتالات (PVC) برای تحقیق در خصوص اثرات مواد افزودنی بر سطح پلاستیک PVC انتخاب شدند و آزمون شناوری برای مطالعه قابلیت شناورماندن PVC روی آنها انجام شد. انرژی آزاد سطح اصلی و صیقل داده شده پلاستیکهای PVC، نشان میدهد که قطعات خرد و تکهتکه شده در سیستمهای شناور، خواص دقیق سطوح پلاستیکی را معرفی میکنند و مواد افزودنی اثرات قابل توجهی بر انرژی آزاد سطح پلاستیکهای PVC دارد. اضافه کردن کربنات کلسیم، نیروی جاذبه یین سطح پلاستیک و آب را بالا برده و در مقابل نیروی پسپندگی بین حبابهای آب و سطح پلاستیک را کاهش و نتیجتاً قابلیت شناوری PVC کاهش مییابد. PnOD نیروی جاذبه ی پین پلاستیک و آب را کاهش و نیروی چسپندگی بین حباب و پلاستیک را افزایش میدهد، بنابراین با بالا رفتن قابلیت شناوری، آبگریزی پلاستیک و آب را کاهش و نیروی چسپندگی بین حباب و پلاستیک را افزایش میدهد، بنابراین با بالا رفتن قابلیت شناوری، آبگریزی پلاستیک افزایش مییابد. آزمون شناوری پلاستیکهای PVC و ضایعات آن نتیجه فوق را تایید کرد. طیف مادون قرمز از میناوری، و توجه به جداسازی پلاستیک و به ویژه بازیافت ضایعات کار اینه کرد، نتیجه گیری فوق بینشی عمیق در خصوص تکنیکهای شناورسازی و توجه به جداسازی پلاستیک و به ویژه بازیافت ضایعات 90 را رائه کرده است.

-مقدمه

پلاستیکها جزو آن دسته موادی هستند که به شکل گستردهای در زندگی روزمره و تولیدات صنعتی مورد استفاده قرار میگیرند. [۱و۲]. در یک دهه اخیر میزان ضایعات پلاستیکی، با توجه به تولید انبوه، مصرف زیاد و عمر کوتاه پلاستیک، به شدت افزایش یافته است. افزون بر این موارد، ضایعات پلاستیکی مشکلاتی همچون آلودگی محیط و اتلاف منابع را به همراه دارند [۳و٤]. بازیافت ضایعات پلاستیکی امکان استفاده مجدد از آن را فراهم ساخته و هزینههای تولید و دفع آن را کاهش میدهد..

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Effects of additives on PVC plastics surface and the natural flotability

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highlights

- The effects of additives on PVC plas-tics surface are investigated.
- The additives have significant impacts on the surface free energy.
- CaCO3 improves the hydrophily and drops the flotability.
- DnOP enhances the hydrophobicity and increases the flotability.
- · Flotation tests were conducted to study the natural flotability of PVC plastics.

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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.



abstract

The polyvinyl chloride (PVC) plastics with calcium carbonate (CaCO3) 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 CaCO3 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

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sharply in recent decades owing to the

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

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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 collec-tion, separation, reprocessing and marketing [5], and separation is the bottleneck at present. Due to their superior intrinsic flota-bility, plastics can be separated by flotation. Compared with the alterative methods, such as electrostatic separation [6,7], sink–float

Table 1 Ingredients of PVC plastics

Ingredients (wt)	Ca ₀	Ca10	Ca ₂₀	Ca ₃₀	Ca40	Ca ₅₀	Ca ₆₀
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 ₀	DP_{10}	DP ₁₅	DP20	DP ₂₅	DP30	DP ₄₀
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 demon-strates 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 (CaCO₃) and di-n-octyl phtha-late (DnOP) are often added in production of plastics to improve the properties of plastics or lower the cost [14-16]. Based on our previ-ous 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 sur-face 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 car-bonate (CaCO3) 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 PVCsho in this paper, respec-tively. 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⁻¹. 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^{-2}) of	various plastic surfaces
---------------------------------------	--------------------------

urface free energy (mJ m) of various	plastic surfac	ces.			De
Surfaces	S	sLW	s ⁺	s	ود کنند
Original surface of PVC resin	48.33	43.41	1.73	3.50	IT'S
Polished surface of PVC	48.28	43.36	1.73	3.49	T S
Original surface of PVC-Ca0	47.39	43.14	1.36	3.32	T G
Polished surface of PVC-Ca0	51.39	46.17	0.84	8.11	ΩΠ
Original surface of PVC-Ca50	47.72	43.22	1.38	3.67	SIL
Polished surface of PVC-Ca50	52.93	46.83	0.50	18.62	
Original surface of PVC-DP0	39.51	36.92	0.41	4.10	
Polished surface of PVC-DP0	44.84	40.66	0.67	6.53	
Original surface of PVC-DP30	37.68	35.98	0.18	4.01	
Polished surface of PVC-DP30	40.13	37.01	0.40	6.07	

Note. S is the total surface free energy of solid, namely the sum of S, S and S.

2.3. Measurement of contact angle

Before the measurement of contact angle, different kinds of sur-faces were prepared to detect the contact angles. Plates of PVC resin and PVC plastics with different content of additives were tailo-red into 20 mm × 20 mm, and then put into tap water containing washing powder, tap water and distilled water in ultrasonic gen-erator (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 x 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 Opti-cal 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].

$$(\overset{LW}{L} + 2 \quad \overrightarrow{L^{+} \quad \overrightarrow{L^{-}}} \quad)(1 + \cos \) = 2(\overset{LW}{S} \quad \overset{LW}{L} + \quad \overrightarrow{S^{+} \quad \overrightarrow{L^{-}}} + \overset{(1)}{\overrightarrow{S^{-} \quad \overrightarrow{L^{+}}}})$$

where is the contact angle between liquid and solid; ^{LW}, ⁺ and 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-Ca₀ and PVC resin may be owing to the effects of low-surface-energy substances such as paraffins, while surface free energy of PVC-Ca50 reflects the impacts of the stabilizers such as lead stearate. The surface free energy of the original surface of PVC-Ca₀ and that of PVC-Ca₅₀ are similar, but the surface free energy of



Fig. 1. The surface free energy of mixed surface as a function of amount of additive.

the polished PVC-Ca₅₀ surface is larger than that of the polished PVC-Ca₀ surface, significantly for Lewis base component. Thus, it can be concluded there exists little CaCO₃ on the surface of PVC plastic, and CaCO₃ will be exposed through polishing.

In the case of DnOP, the difference in surface free energy between both the polished and original surface of PVC-DP₀ and that of PVC resin may be due to the effects of other additives such as dibutyl phthalate, which reduce the surface free energy. The change between the original and polished surface of PVC-DP₃₀ indicates that DnOP tends to be gathered on the surface of plastic and thus decreases the surface free energy.

Owing to the "surface enrichment" effects, the surface of plastic does not exhibit the true performance of polymer resin and additives. Such additive as CaCO₃ or DnOP will increase or decrease the surface free energy of plastic. Moreover, the original surface of plastic will be destroyed during the process of crushing or shredding, and thus the effects of additives on surface properties of plastic should be investigated for plastic flotation.

3.1.2. The effects of additives on surface free energy of mixed surface

The surface of plastic can be viewed as the mixed surface composed of polymer resin and additive. Supposing that additive are distributed evenly in the plastics and substituting the volume percentage of additive for area percentage, the relationships between surface free energy of the mixed surface and content of additive were obtained, and details on the calculations are presented in supplementary material. The surface free energy of PVC-CaCO₃ and PVC-DnOP surfaces as a function of amount of additive is demonstrated in Fig. 1.

As shown in Fig. 1, it is illustrated that the increase of the amount of CaCO₃ has little effect on the LW component and the total surface



Fig. 2. The solid-liquid interaction free energy as a function of the amount of additive in aqueous medium.

free energy, and, meanwhile, Lewis acid component is considerable low and tends to decrease slightly. However, the Lewis base component increases significantly with increasing of amount of CaCO₃ and thus the mixed surface is further developed into unipolar surface. Unlike CaCO₃, the addition of DnOP reduces the total surface free energy, and parameters of surface free energy all decrease slightly.

3.1.3. The interactions between the mixed surface and water The total interaction energy G^{LW -AB} between the mixed sur-

face equals the sum of LW interaction free energy G_{SW}^{LW} and Lewis acid–base (AB) interaction free energy G_{SW}^{AB} . According to Eqs. (S4) and (S5) presented in supplementary materials, the relationships between the solid–liquid interaction free energy and the amount of additive in aqueous medium are shown in Fig. 2.

As demonstrated in Fig. 2, the addition of CaCO₃ has little impact on LW interaction free energy but increases AB interaction free energy, which results from the significant increase of Lewis base component. As a result, there is a remarkable rise in the total interaction free energy, which implies that the attraction force between mixed surface and water increases and the hydrophilicity of plastic surface is improved. However, the solid–liquid interactions increase with increasing of the amount of DnOP, which is owing to that the addition of DnOP reduces the total surface free energy. Furthermore, the negative value of the solid–liquid interactions indicates that the interaction force between the mixed surface and water are attraction forces. And thus the attraction force between mixed surface and water decreases and the hydrophobicity of plas-

tic is improved.



Fig. 3. The interactions between the mixed surface and bubble as a function of the amount of additives.

3.1.4. The interactions between the mixed surface and bubble

Based on the extended DLVO theory [21,22], the interactions between two components include LW interaction free energy, AB interaction free energy and electrostatic interaction free energy. According to our previous study [17], action distance of electro-static force is significantly limited, while AB free energy is the dominant factor of the interactions between the mixed surface and bubble in aqueous medium. Thus, the effects of LW and AB on the interaction between the mixed surface and bubble are further dis-cussed. Based on Eqs. (S6) and (S7) presented in the supplementary materials, the interactions between the mixed surface and bubble in aqueous medium are shown in Fig. 3.

As exhibited in Fig. 3, the van der Waals force between the mixed surface and bubble is repulsive force, which increases with increas-ing of the amount of CaCO₃ but decreases with decreasing of the amount of DnOP. The LW interaction between the mixed surface and bubble leads to hydrophobic attraction, whose value decreases significantly with increasing of the amount of CaCO₃ but increases with increasing of the amount of DnOP. Under the effects of LW–AB interactions, the addition of CaCO₃ impairs the adhesion of bubble on the mixed surface, and thus reduces the flotability of plastic particles, while the addition of DnOP enhances the adhesion of bubble on the mixed surface and thus improves the flotability of plastic particles.

3.2. The natural flotability of PVC plastics

The natural flotability of PVC plastics with additives are shown in Fig. 4a. It is obvious that the PVC plastics with DnOP serving as additive possess good natural flotability, and the flotation recov-ery keeps constant, namely 100%, with increasing the amount of DnOP. This is because PVC resin has superior natural flotability and



Fig. 4. The natural flotability of PVC plastics: (a) PVC with additives; (b) waste plastics.

the addition of DnOP enhances the flotability further. However, the addition of CaCO₃ changes markedly the flotability of PVC plastic. The flotation recovery remains 100% when the percent of CaCO₃ is less than 20 wt.%, and then decreases remarkably with increasing of the CaCO₃, which can be attributed to that the addition of CaCO₃ enhances the hydrophily of plastic, and thus reduces the flotability.

The natural flotability of waste PVC plastics were further stud-ied, and the result is demonstrated in Fig. 4b. The flotation recovery of PVC-dec, which contains larger percent of CaCO₃, is considerably small, while that of PVC-sho containing larger percent of DnOP is 100%. From the infrared spectrum (Fig. 5) of the two waste plastics, it is observed that CaCO₃ and DnOP have a great impact on the PVC plastics. Therefore, it can be concluded that the PVC plastics were influenced significantly by the additives.

4. Conclusion

Comparing the original and polished surface of PVC plastics, it is demonstrated that the shredded plastic particle in flotation system reflects the surface property of plastics and the additives have con-spicuous effects on the surface free energy. The addition of CaCO₃ leads to an increase of the interaction free energy between the PVC-CaCO₃ surface and bubble in aqueous medium. CaCO₃ increases the attraction force between the mixed surface and water but decreases noticeably hydrophobic attraction between particle and bubble, and thus it reduces the flotability of PVC plastic.

The total surface free energy of PVC-DnOP surface decreases with increasing the amount of DnOP. The total interaction free

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Fig. 5. Infrared spectrum of PVC plastics and additives.

energy between the mixed surface and water decreases and the interaction free energy between the mixed surface and bubble increase slightly. The attraction force between particle and water is weakened, but the hydrophobic attraction between particle and bubble is enhanced, and thus DnOP improves the flotability of PVC plastic.

The flotation tests of PVC plastics confirm the effects of additives on the natural flotability of PVC plastics. Flotation recov-ery decreases significantly with increasing of the amount of CaCO₃, while that of PVC plastic remains 100% with increasing of the amount of DnOP. Flotation recovery of waste PVC plastics with different additives demonstrates remarkable dif-ference, and the infrared spectrum verifies the influence of the additives.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2013 .10.010.

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