Physicochem. Probl. Miner. Process., 62(5), 2026, 242708

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049
© Wroclaw University of Science and Technology

Surface characterization and flotation behavior of virgin PP and HDPE in the presence of diethylene glycol dibenzoate and lignin alkaline

Cemal Cem Bakır, Zeynep Üçerler-Çamur, Tülay Türk, Murat Olgaç Kangal

Mineral Processing Engineering Department, Faculty of Mines, Istanbul Technical University, Maslak, Istanbul 34469, Türkiye

Corresponding author: bakir19@itu.edu.tr (Cemal Cem Bakır)

Abstract: Plastics are widely used materials whose global production has increased dramatically, reaching 413.8 million tons, and is projected to triple by 2060. This growth has led to a significant rise in plastic waste, posing environmental challenges. Conventional disposal methods such as landfilling and incineration are not environmentally friendly, as they may cause ecosystem damage and toxic gas emissions. Therefore, plastic recycling has become a crucial option from both waste management and production perspectives. Plastic recycling generally involves collection, separation, size reduction, washing, and reprocessing stages, all of which strongly influence final product quality. Effective recycling requires accurate separation of plastics. Although manual and density-based separation methods are commonly used, they are insufficient for systems with similar densities, such as HDPE–LDPE or PVC–PET–POM mixtures. In such cases, flotation offers an effective alternative. Flotation exploits differences in surface chemical properties and wettability, enabling selective separation through surface modification using appropriate reagents. The efficiency of flotation is influenced not only by surface chemistry but also by the density, size, and shape of plastic particles. In this study, the selective separation of mixed plastic systems consisting of HDPE and PP was investigated using flotation-based techniques. Surface physicochemical properties of the plastics and reagents were systematically characterized using surface tension measurements, contact angle measurements, and micro-flotation tests to evaluate their wettability and surface charge behavior. The effects of surface conditioning and flotation parameters on separation efficiency were examined, and the relationship between surface characteristics and flotation response was discussed in detail.

Keywords: plastic, flotation, surface chemistry, recycling

1. Introduction

Plastics utilize hydrocarbons sourced from natural resources such as petroleum and natural gas. Plastics are created by polymerizing monomers via chemical bonding (Mills et al., 2020). The plastics industry has experienced continuous global growth over recent decades. Driven by rising industrial demand, global plastic production has reached approximately 460 Mt annually, while global circular plastics production accounts for only 44.2 Mt (approximately 9.6% of total output). Polyolefins continue to dominate worldwide production, with polyethylene (PE) and polypropylene (PP) together accounting for more than 50% of total plastic manufacturing. Other major polymers include polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). Despite increasing environmental awareness and circularity targets, over 70% of post-consumer plastic waste continues to be disposed of through landfilling or incineration. This persistent imbalance between primary production and circular recycling underscores the growing environmental burden of plastic materials (Plastics Europe, 2026).

Despite the continuous growth of the plastics industry, the transition toward a circular plastics economy remains limited. This limitation is mainly due to technical difficulties in sorting complex and mixed plastic streams, high collection costs, and property degradation during mechanical reprocessing. According to Plastics Europe (2023), only approximately 9.6% of global plastic production originated

DOI: 10.37190/ppmp/242708

from circular sources, with over 90% derived from fossil feedstocks. More recently, Plastics Europe (2026) reported that circular plastics accounted for 15.8% of total European production, yet more than 84% remained fossil-based and over 70% of post-consumer waste was still landfilled or incinerated. The current recycling rate remains insufficient compared with the continuously increasing demand for plastic materials.

The continuous increase in plastic waste has made the development of efficient recycling technologies essential for sustainable resource recovery (Hopewell et al., 2009). Driven by population growth, economic development, and expanding industrial applications, global plastic production has continued to increase steadily over recent decades (Geyer et al., 2017).

According to the Organization for Economic Co-operation and Development (OECD) (2022), global plastic production is projected to nearly triple by 2060 under a business-as-usual scenario. Without substantial improvements in recycling technologies and circular economy practices, plastic waste generation is expected to increase proportionally, placing additional pressure on environmental systems worldwide.

Since a considerable proportion of plastic products are used in short-life applications, particularly packaging, increasing plastic demand directly contributes to the rapid growth of post-consumer plastic waste. These trends highlight the need for efficient recycling and separation technologies that can recover valuable polymers from mixed plastic waste.

Among the various plastic separation techniques, froth flotation has emerged as one of the most promising methods for recovering valuable polymers from mixed plastic waste. Unlike conventional density-based separation techniques (such as sink-float), froth flotation exploits differences in the surface wettability of plastics, enabling the selective separation of polymers with similar densities. Consequently, numerous studies have focused on modifying the surface properties of plastics through chemical conditioning, wetting agents, and depressants to enhance flotation selectivity (Fraunholcz, 2004; Shen et al., 2002; Burat et al., 2009).

Previous studies have demonstrated that selective froth flotation is an effective technique for separating polypropylene (PP) and high-density polyethylene (HDPE) by exploiting differences in their surface properties.

Üçerler and Kangal (2018) investigated the selective flotation separation of polypropylene (PP) and high-density polyethylene (HDPE) using a modified short-column flotation cell after alkaline conditioning with sodium hydroxide. Calcium lignosulfonate (CaLS) was used as a selective wetting agent, while methyl isobutyl carbinol (MIBC) served as the frother. The results showed that CaLS preferentially increased the hydrophilicity of HDPE with only a limited effect on PP, enabling the selective flotation of PP. Under the optimum conditions, PP and HDPE were successfully separated with a PP product purity of 98.2% and a recovery of 99.8%, demonstrating the effectiveness of selective surface modification for polyolefin flotation.

The selective flotation method for separating PET and HDPE used in drinking water bottles was studied by Kangal (2010). Several conditions were examined in this study, including the temperature and duration of the NaOH conditioning, the types and concentrations of the reactive, pH, and the reactive's conditioning period. In summary, 100% HDPE was effectively separated from PET with 99.6% efficiency (Kangal, 2010).

Although numerous studies have investigated the flotation separation of mixed plastic wastes, most published research has focused on separating polyethylene terephthalate (PET) and polyvinyl chloride (PVC) from each other or from other polymers through various surface modification strategies (Kökkılıç et al., 2022). For instance, Nagy et al. (2011) and Pita and Castilho (2020) demonstrated that alkaline pre-treatment (NaOH) selectively increases PET hydrophilicity, enabling efficient separation from PVC and other plastics such as PS, PMMA, and PC. Similarly, advanced chemical pre-treatments, such as surface micro-alcoholysis (Zhao et al., 2019), KOH-catalyzed ethylene glycol treatment (Wang et al., 2020), and selective $CaCO_3$ coating (Zhang et al., 2020), have been successfully applied to separate PET from PVC, ABS, and PC mixtures with purities and recoveries often exceeding 99%. In addition to chemical surface modifications, selective flotation of post-consumer PET and PVC has also been achieved using specific plasticizers and wetting agents without prior alkaline treatment. Notably, Yenial et al. (2013) evaluated diethylene glycol dibenzoate (DIB) and achieved highly selective separation for PET/PVC mixtures.

Similarly, Yuce and Kilic (2015) successfully used alkaline lignin (LA) as a selective plasticizer to separate PET and PVC in column flotation. However, while these strategies and reagents (such as DIB and LA) are highly effective for polar plastics, comparatively fewer studies have addressed the flotation separation of non-polar polyolefin systems such as PP and HDPE, despite the greater challenge arising from their highly similar physicochemical properties. This difference stems from the surface chemistry of the polymers. Unlike PET and PVC, which contain polar ester groups and chlorine atoms that promote selective reagent interactions, PP and HDPE are purely non-polar hydrocarbons without functional groups. Therefore, conditioning agents interact with both polyolefins mainly through non-specific hydrophobic forces, making selective wetting inherently more difficult. Evaluating whether reagents commonly used for PET and PVC (such as DIB and LA) can provide sufficient selectivity for polyolefins is critical to understanding the limits of reagent-assisted flotation. Accordingly, this study systematically examines the interfacial behaviour and flotation response of virgin PP and HDPE using DIB and LA.

2. Materials and methods

2.1. Materials

Arçelik A.Ş. supplied virgin PP and HDPE granules with particle sizes of -3.36 mm + 2 mm. Although both are white, the two polyolefins have different optical properties. Compared to HDPE, PP is much more translucent. Additionally, the cylindrical shape of HDPE granules and the spherical shape of PP granules make it easier to identify the experimental products visually. Virgin plastic samples utilized in micro-flotation and virgin plastic sheets used for contact angle measurements are shown in Fig. 1. For the contact angle measurements, virgin, unpigmented, colourless sheet-form plastics with the smoothest possible surface texture were obtained. These plastic sheets, in PP and HDPE types, were supplied by Filiz Plastik Metal San. Tic. A.Ş. and Polser Polimer, respectively.



Fig. 1. Virgin plastic samples and sheets

Analytical-grade sodium hydroxide (NaOH) and hydrochloric acid (HCl) were utilized for alkaline surface conditioning and pH adjustment, respectively. All experimental solutions were prepared using distilled water with a reference surface tension of 72.8 mN/m at 20 °C. Di(ethylene glycol) dibenzoate (DIB, $C_{18}H_{18}O_5$) obtained from Sigma-Aldrich Corp. (USA) was used as a plasticizer. DIB is a dibenzoate ester-based compound consisting of two benzoate aromatic rings linked by a central diethylene glycol chain, with a molecular weight of 314.33 g/mol and a density of 1.175 g/mL at 25 °C. Owing to its hydrophobic aromatic rings and intermediate ester linkages, DIB has low water solubility (0.038 g/dm^3 at 20 °C) and is a clear, viscous liquid under ambient conditions (dynamic viscosity of 83–111 mPa·s). The chemical structure of DIB is shown in Fig. 2.

Alkaline lignin (LA, low sulfonate content) was obtained from Sigma-Aldrich Corp. (USA) and used as a surface-modifying dispersing agent. LA is a biopolymeric macromolecule derived from the alkaline

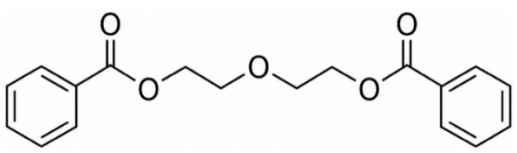


Fig. 2. Typical structure of DIB

kraft pulping of lignocellulosic biomass, possessing an average molecular weight of approximately 10,000 g/mol and a sulfur content of around 4%. Its chemical structure consists of an aromatic phenylpropane skeleton functionalized with hydrophilic hydroxyl (OH), methoxy (OCH_3), and sulfonate (SO_3^-) groups, making it water-soluble and yielding an alkaline pH of approximately 10.5 in a 3 wt.% aqueous solution. The typical chemical structure of LA is illustrated in Fig. 3.

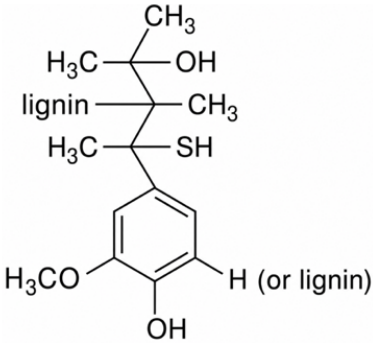


Fig. 3. Typical structure of LA

2.2. Methods

To investigate the interactions between the plastics and the reagents mentioned in the materials section, a series of surface chemistry studies was conducted. These studies included surface tension measurements of the reagents, contact angle measurements of virgin plastic sheets, and micro-flotation tests.

2.2.1. Surface tension measurements

Surface tension measurements were performed using a Krüss K-8 tensiometer based on the Du Noüy ring method. First, the setup was calibrated by measuring distilled water, whose surface tension is known. The value obtained with distilled water was 72.8 mN/m, as reported in the literature. Measurements were then performed with new solutions prepared from 10% DIB and LA solutions at mol/dm^3 concentrations of 10^0, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}, respectively. The surface tensions of these reactants at these concentrations were also measured at pH levels of 4, 6, 8, and 10. Measurements were taken three times for each condition, and the average was calculated.

2.2.2. Contact angle measurements

Contact angle measurements were carried out using a Dataphysics OCA 15EC (Stuttgart, Germany) based on the Sessile Drop Method. The virgin plastic plates mentioned in the materials section were used for contact angle measurement. Prior to reagent conditioning, the plastic plates were subjected to an alkaline pre-treatment using 1 mol/dm^3 NaOH for 5 min. Solutions were prepared at concentrations ranging from 10^{-5} to 10^{-1} mol/dm^3 for each reagent. These solutions were placed in a beaker with the pre-treated plastic plates, and the plates were conditioned for 5 min. Solutions were prepared at different pH values (4, 6, 8, and 10) using NaOH and HCl for each reagent concentration, as well as distilled water. The contact angle measurement conditions were summarized in Table 1.

Table 1. The contact angle measurement conditions

Methodology	Reagents	pH	Concentration	Conditioning Time
Prior to contact angle measurements, the plastic samples were subjected to an alkaline pre-treatment (1 mol/dm3 NaOH for 5 min) and then conditioned with reagents for 5 min to modify their surface properties.	Distilled Water			
	DIB	4	From 10^{5-} to 10^{1-} mol/dm^3	5 min.
		6		
		8		
	LA	10		

After conditioning, the virgin plastic plates were left to dry at room temperature. After drying, the plastic plates were placed on the sample stage of the contact angle measuring instrument. A fixed droplet of distilled water (2.0 ± 0.2 μL) was automatically dosed onto the substrate surface using a motorized micro syringe to eliminate gravitational droplet distortion and ensure volume consistency. Images of the sessile drop were captured by the integrated digital camera, and the static contact angles (θ_{left} and θ_{right}) were determined using Young–Laplace (or ellipse-fitting) analysis in the device software. For each experimental condition, measurements were performed across ten distinct locations on the conditioned sheet, and the arithmetic mean was calculated to represent surface wettability. Furthermore, to ensure reproducibility, selected experiments were repeated three times.

2.2.3. Micro-flotation tests

The virgin plastics in granular form mentioned in the materials section were used in micro-flotation experiments. 1 gram of each pure plastic was used for each micro-flotation experiment. Solutions were prepared at concentrations of 10^{1-}, 10^{2-}, and 10^{3-} mol/dm^3 for each reagent used in the micro-flotation tests. Before the micro-flotation tests, the virgin plastic samples were subjected to alkaline treatment for 5 min by mixing with 20 cm^3 of 1 mol/dm^3 NaOH solution at 750 rpm to achieve approximately 5% pulp content, thereby altering their surface properties. After 5 min of alkaline pre-treatment, the plastic samples were filtered, washed with distilled water, and then transferred into a beaker containing the pre-prepared reagent solution. The solution volume was set to 180 cm^3 to match the tube volume. The alkaline-treated pure plastics were conditioned in the solution for 5 min. At this point, the optimum pH values for each reagent, determined based on the surface tension and contact angle measurements conducted earlier in this study, were tested. After a 5 min conditioning period, the solution in the beaker and the conditioned virgin plastics were transferred into a tube. Nitrogen gas was used instead of ambient air to ensure precise control of the gas flow rate. A hose connected to the nitrogen tank supplied air, with the other end attached to the tube. The air supply to the system was then adjusted to 25 cm^3/min using a flowmeter. Simultaneously, the stirrer and air supply were activated, and flotation was performed for 5 min. Eventually, the float products were collected from the upper channel of the tube. Floatability of the plastics was determined based on the masses of the float and sunken products. The following equation (Eq. 1) was used to calculate floatability.

$$\text{Floatability } (\%) = \frac{m_{float}}{m_{float}+m_{sunken}} x100 \quad (1)$$

where m_{float} and m_{sunken} represent the dried mass of the float and sunken products, respectively. The micro-flotation experimental conditions are summarized in Table 2, and a schematic representation of the micro-flotation process is given in Fig. 4.

Table 2. The micro-flotation test conditions

Methodology	Reagents	pH	Concentration	Conditioning Time	Flotation Time	Aeration Rate
Prior to micro-flotation tests, plastic samples were subjected to alkaline treatment using 1 mol/dm^3 NaOH solution for 5 min to modify their surface properties.	DIB LA	4 6 8	From 10^{-3} to 10^{-1} mol/dm^3	5 min	3 min	25 cm^3/min.

3. Results and discussion

3.1. Surface tension measurements

Surface tension measurements were performed to determine the interfacial activity of DIB and LA solutions across different concentrations and pH levels, as reagent adsorption at the air–water interface strongly governs foam stability and flotation selectivity. The surface tension results for DIB and LA are presented in Figs. 5 and 6, respectively.

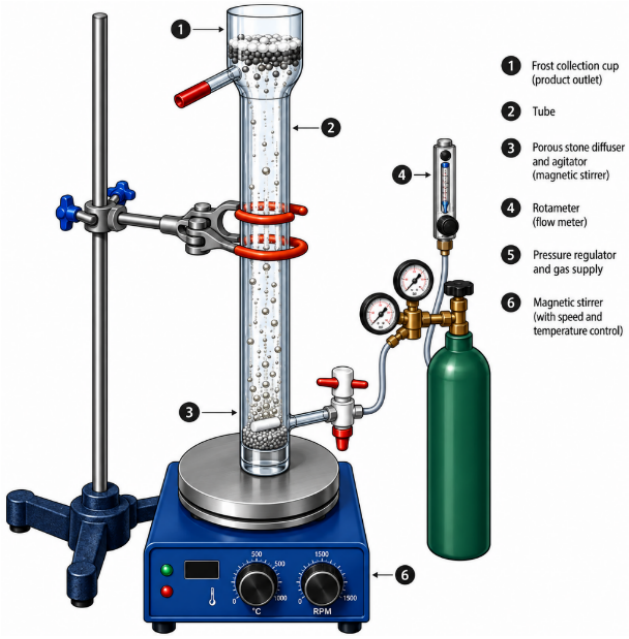


Fig. 4. Schematic illustration of micro-flotation test procedure

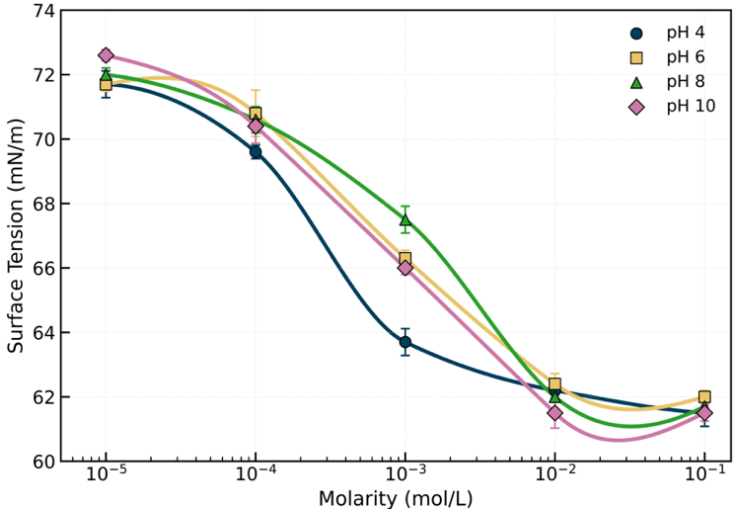


Fig. 5. Surface tension measurements performed with DIB

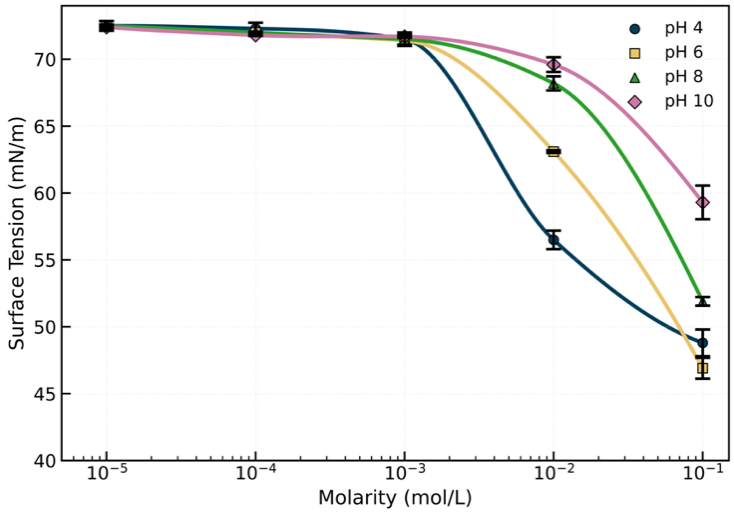


Fig. 6. Surface tension measurements performed with LA

DIB had a relatively limited effect on surface tension compared with the other reagents investigated in this study. Surface tension decreased moderately from approximately 72 mN/m to 61 mN/m with increasing concentration, while only minor variations were observed across different pH conditions. This pH-independent behavior occurs because DIB lacks ionizable functional groups, meaning its chemical form remains stable regardless of pH changes in the aqueous phase. Conversely, the moderate decrease in surface tension with increasing concentration is driven by DIB's low water solubility and hydrophobic aromatic rings, which physically force the molecules to accumulate at the air-water interface. These results indicate that DIB exhibits relatively weak interfacial activity and a limited tendency to adsorb at the air–water interface compared with conventional surfactants, primarily because it lacks a distinct amphiphilic structure with a strong polar head and a long hydrophobic tail.

Fig. 6 shows the effect of LA concentration on the solution's surface tension at different pH values. At low LA concentrations (10^{-5}–10^{-3} mol/dm^3), the surface tension remained nearly constant at approximately 72–73 mN/m for all pH values, indicating that the reagent had little influence on the air–water interface in this concentration range. As the LA concentration exceeded 10^{-3} mol/dm^3, the surface tension decreased noticeably across all pH conditions. The decrease was most pronounced at pH 4 and 6, whereas a more gradual reduction was observed at pH 8 and, particularly, at pH 10. At the highest concentration (10^0 mol/dm^3), the lowest surface tension value was obtained at pH 8 (approximately 41 mN/m), while pH 10 exhibited the highest surface tension (approximately 47 mN/m). Overall, the results indicate that LA exhibits concentration-dependent surface activity, with the pH effect becoming more pronounced at higher reagent concentrations.

Similar to the findings of Güney et al. (2015), increasing LA concentration resulted in a pronounced decrease in surface tension, whereas DIB exhibited a comparatively weaker effect. Likewise, LA showed a greater ability to reduce the surface tension of the solution than DIB, which can be attributed to its amphiphilic macromolecular structure containing both a hydrophobic aromatic backbone and strongly hydrophilic sulfonate/hydroxyl groups. From a flotation perspective, such a drastic reduction in liquid surface tension indicates increased froth stability, but it also alters the thermodynamic driving force for bubble-particle attachment. However, Güney et al. (2015) reported that liquid surface tension alone cannot adequately explain flotation selectivity and suggested that changes in polymer surface characteristics should also be considered. Although liquid surface tension does not solely dictate selective separation, measuring it remains a mandatory fundamental step in this study to determine the frothing capabilities and the thermodynamic state of the liquid-gas interface for these specific reagents. Therefore, contact angle measurements were also evaluated to better understand the solid-liquid interaction between the reagents and polymer surfaces.

3.2. Contact angle measurements

Contact angle measurements were conducted to evaluate the wettability characteristics of PP and HDPE surfaces after conditioning with different reagents. Because flotation performance is strongly influenced by particle surface hydrophobicity, contact angle measurements provide valuable information on interactions between reagents and plastic surfaces. Changes in contact angle values indicate changes in surface wettability, with higher contact angles indicating increased hydrophobicity and lower contact angles indicating enhanced hydrophilicity. Therefore, the obtained results can contribute to understanding the adsorption behavior of the investigated reagents and their potential effects on flotation performance. In this context, the results of contact angle measurements for distilled water, DIB, and LA reagents are shown in Figs. 7, 9, and 11, respectively. Tables 3, 4, and 5 present the contact angle values for these reagents.

Table 3. Contact angle values in distilled water

Plastic Type	pH			
	4	6	8	10
PP	95.48	93.03	98.74	88.90
HDPE	94.13	93.43	129.04	128.54

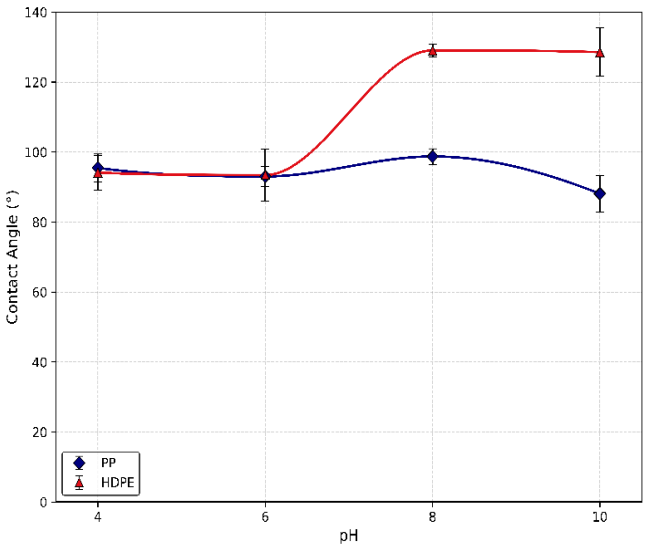


Fig. 7. Contact angle results for distilled water

Contact angle measurements in distilled water showed that two plastics exhibited hydrophobic behavior across the investigated pH range. HDPE showed the highest contact angles, reaching approximately 129° at pH 8 and 10, indicating the strongest hydrophobicity among the tested plastics. PP maintained contact angles between approximately 88° and 99°. Notably, the contact angles measured for HDPE in distilled water at pH 8 and 10 were higher than typical literature values (90°–105°). This increase is directly attributed to the alkaline pre-treatment applied to the plastic sheets before measurement. Consequently, these elevated values reflect the specific wettability of the alkali-pre-treated HDPE surfaces rather than the baseline state of completely untreated virgin HDPE. Overall, the results confirm the inherent hydrophobicity of the investigated plastics and provide a reference for evaluating the effects of the conditioning reagents.

The contact angle values obtained in distilled water are generally consistent with those reported in the literature for PP (90°-102°) and HDPE (90°-105°) (Brighton Technologies Group, 2023). Previous studies have also reported water contact angles for virgin polyolefins within a similar range. Karaagac et al. (2021) measured water contact angles of 97.6° for virgin PP and 78.4° for virgin HDPE using the sessile drop technique. Likewise, Bolte et al. (2024) reported water contact angles of 92° for virgin PP and 94° for virgin HDPE, demonstrating that both polymers exhibit highly hydrophobic surfaces. However, the measured values may vary depending on material grade and experimental conditions. Among the investigated plastics, HDPE exhibited the highest hydrophobicity, whereas PP showed lower contact angles. Minor deviations from literature data may be attributed to differences in material source, surface condition, and sample preparation procedures. Fig. 8 shows contact angle pictures in the presence of distilled water taken from the device.

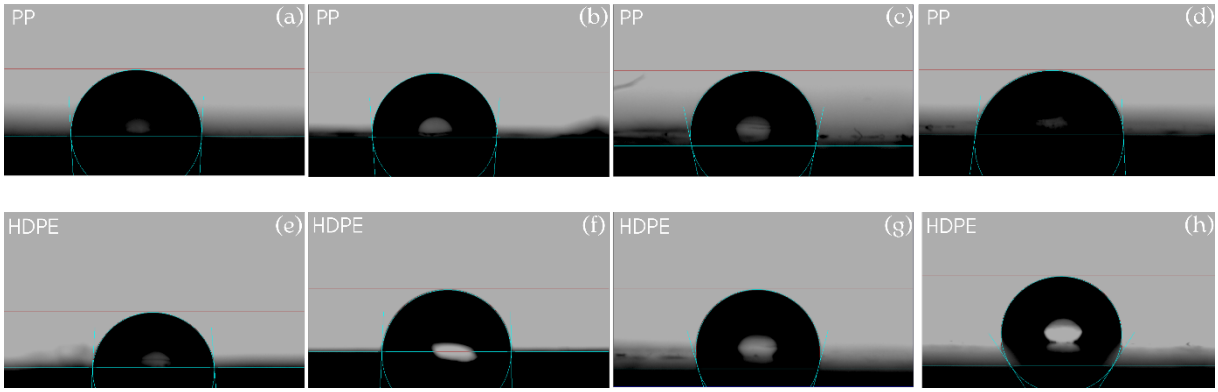


Fig. 8. Representative contact angle images of PP and HDPE obtained at different pH values in the presence of distilled water. **(**a–d) PP at pH 4, 6, 8, and 10, respectively; (e–h) HDPE at pH 4, 6, 8, and 10, respectively

Table 4. Contact angle values in DIB

Plastic Type	Molarity (mol/dm³)	pH			
		4	6	8	10
PP	10^{-5}	101.06	100.13	101.54	101.97
	10^{-4}	98.29	95.63	97.25	95.18
	10^{-3}	95.39	95.53	96.94	94.88
	10^{-2}	93.71	92.19	92.55	90.28
	10^{-1}	70.39	71.97	70.99	81.86
HDPE	10^{-5}	103.30	102.87	100.58	101.38
	10^{-4}	94.73	96.57	94.75	94.85
	10^{-3}	94.33	92.32	93.43	91.18
	10^{-2}	91.06	90.35	92.19	90.31
	10^{-1}	71.68	70.74	74.55	73.34

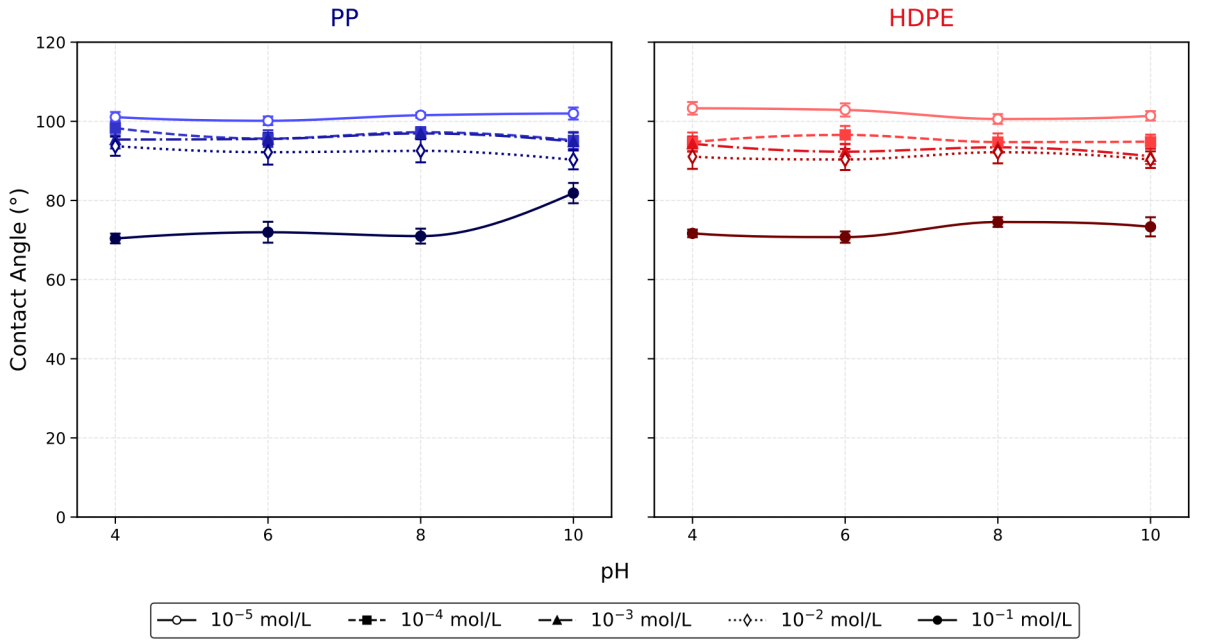


Fig. 9. Contact angle results for DIB

Compared with other reagents, DIB produced only minor changes in the contact angles of PP and HDPE. The measured contact angles remained relatively close to those obtained in distilled water, particularly for PP and HDPE, which maintained values above 90° under most experimental conditions. Although slight variations in pH and concentration were observed, surface hydrophobicity did not decrease substantially. Therefore, DIB exerted only a limited influence on the wettability of the investigated plastics. Representative contact angle images of PP and HDPE obtained using the DataPhysics OCA 15EC are presented in Fig. 10.

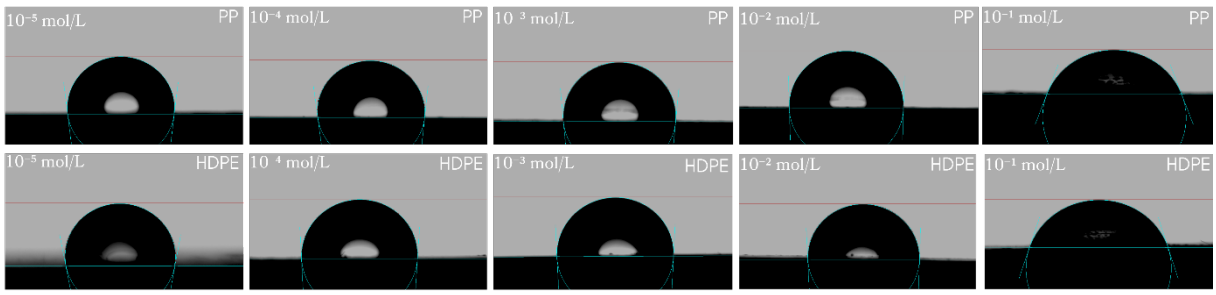


Fig. 10. Representative contact angle images of PP and HDPE in the presence of DIB

Table 5. Contact angle values in LA

Plastic Type	Molarity (mol/dm³)	pH			
		4	6	8	10
PP	10^{-5}	76.56	92.77	96.08	89.91
	10^{-4}	72.86	80.35	87.05	80.24
	10^{-3}	50.70	68.12	74.70	77.60
	10^{-2}	8.13	8.91	74.56	76.39
	10^{-1}	8.04	8.11	64.38	75.93
HDPE	10^{-5}	9.81	98.07	100.96	79.95
	10^{-4}	79.70	88.02	92.81	64.92
	10^{-3}	79.39	84.06	89.84	50.69
	10^{-2}	17.47	78.31	17.76	20.12
	10^{-1}	8.69	19.09	16.65	14.15

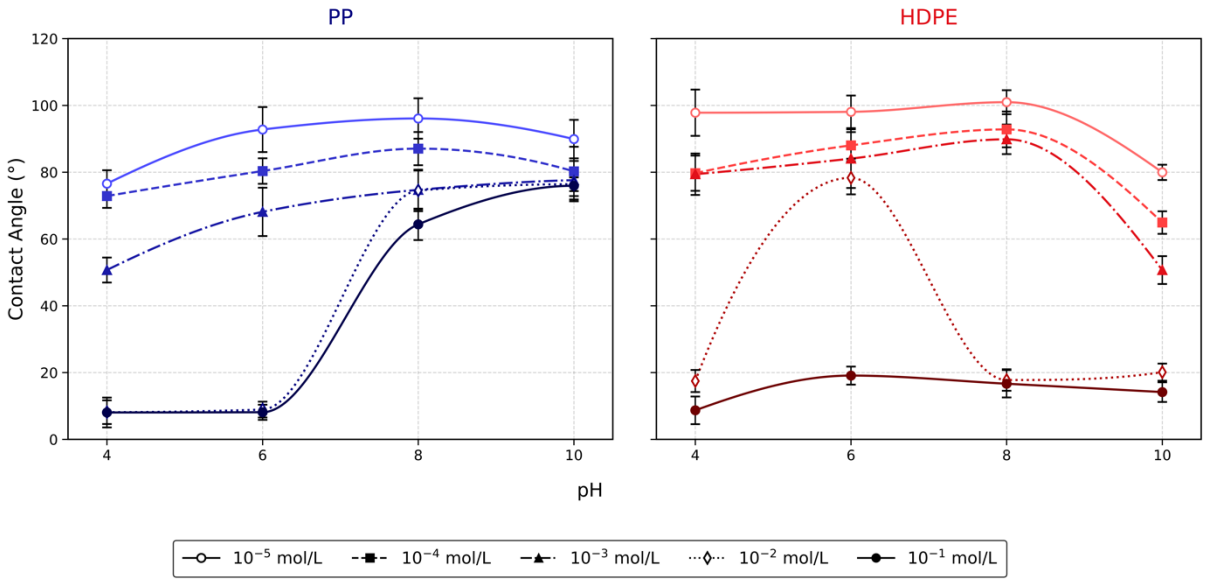


Fig. 11. Contact angle results for LA

Lignin alkaline significantly affected the wettability of the plastic surfaces, especially at elevated concentrations. A gradual decrease in contact angle was observed as reagent concentration increased for all plastics. The effect was particularly pronounced at concentrations of 10^{-2} and 10^{-1} mol/dm³, where contact angles decreased considerably compared with those measured in distilled water. The results suggest that alkaline lignin effectively modified the surface properties of the plastics and promoted a more hydrophilic surface character.

No previous study directly investigated the contact angle behavior of untreated virgin PP and HDPE in the presence of DIB and LA under comparable experimental conditions. Therefore, relevant studies reporting the effects of DIB and LA on different polymer surfaces, together with studies examining the influence of various surfactants on the contact angle of untreated virgin PP and HDPE, were considered to interpret the results obtained in the present study.

Sritapunya et al. (2012) investigated the effects of cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS), sodium octyl benzene sulfonate (SOBS), and 1-octanol (C8) on the wettability of virgin HDPE. The authors reported that all of these reagents reduced the contact angle of HDPE to varying extents, indicating increased surface hydrophilicity. Similarly, increasing LA concentration decreased the contact angle of HDPE in the present study, suggesting enhanced wettability of the polymer surface.

Different surfactants have also been reported to reduce the contact angle of untreated virgin PP, thereby enhancing its surface wettability. Dutschk et al. demonstrated that SDS, DTAB, dodecyl trimethyl ammonium sulfate (DTAS), and pentaethylene glycol mono dodecyl ether ($C_{12}E_5$) all decreased the contact angle of virgin PP, indicating that various reagents can increase the hydrophilicity of untreated PP surfaces.

While these literature findings demonstrate that conventional surfactants can successfully increase the hydrophilicity of non-polar polyolefins, the pronounced differences observed between DIB and LA in the present study must be explained by their specific molecular structures and resulting adsorption mechanisms. Polyolefins, such as PP and HDPE, have non-polar, highly hydrophobic hydrocarbon chains. Consequently, reagent attachment to these surfaces is primarily driven by hydrophobic interactions and van der Waals forces.

DIB is an ester-based plasticizer containing hydrophobic aromatic rings, but it lacks strongly ionizable or highly polar functional groups. Although the aromatic rings of DIB can weakly attach to the polyolefin surfaces through hydrophobic interactions, the molecule does not expose strong hydrophilic groups to the aqueous phase. Without highly polar groups to interact with water molecules, DIB fails to create a stable hydration layer at the solid-liquid interface, explaining why the contact angles of both PP and HDPE remain high.

In contrast, alkaline lignin (LA) is a strongly amphiphilic macromolecule. Its structural framework consists of a hydrophobic aromatic (phenylpropane) backbone heavily functionalized with highly polar and ionizable groups, particularly hydroxyl and sulfonate groups. When LA is added to the solution, its hydrophobic aromatic backbone strongly adsorbs onto the non-polar PP and HDPE surfaces. Simultaneously, the strongly hydrophilic hydroxyl and sulfonate groups are forced to face outward toward the aqueous phase. This proposed adsorption configuration may expose hydrophilic functional groups to the aqueous phase, thereby increasing the wettability of the plastic surfaces.

Güney et al. (2015) reported that both DIB and LA increased the contact angle of PET while decreasing that of PVC, with LA producing a more pronounced reduction in the contact angle of PVC than DIB. These changes created a greater wettability difference between PET and PVC, which was associated with improved flotation selectivity.

Representative contact angle images of PP and HDPE obtained using the DataPhysics OCA 15EC are presented in Fig. 12.

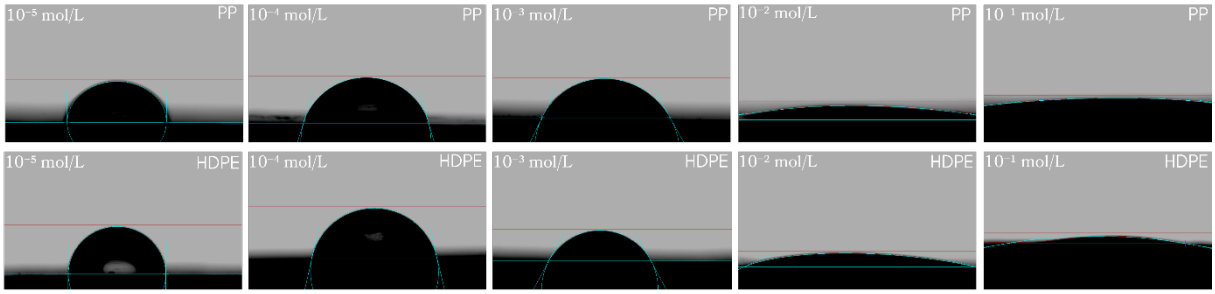


Fig. 12. Representative contact angle images of PP and HDPE in the presence of LA

3.3. Micro-flotation experiments

Micro-flotation experiments were conducted to evaluate the floatability of polypropylene (PP) and high-density polyethylene (HDPE) using two different reagents at varying pH levels. The obtained floatability values were analyzed to evaluate the effects of reagent type and concentration on the flotation behavior of the investigated virgin plastics. The ranges of 10^{-3} and 10^{-1} mol/dm^3 were selected based on the surface tension and contact angle results where significant changes in interfacial behaviour were initiated around 10^{-3} mol/dm^3. The micro-flotation test results for the DIB and LA reagents are presented in Figs. 13 and 14, respectively. Additionally, Tables 6 and 7 summarize the micro-flotation results for the DIB and LA reagents.

DIB exhibited the weakest influence on the floatability of the investigated plastics. PP and HDPE maintained floatability values close to 100% across the entire concentration range, indicating that DIB did not significantly alter their flotation behavior. Overall, DIB caused no changes in floatability and

therefore showed limited ability to modify flotation. As a result, DIB is not effective in separating virgin plastics.

Table 6. Micro-Flotation results of DIB at different pH levels

pH	Molarity (mol/dm³)	PP Floatability (%)	HDPE Floatability (%)
4	10^{-3}	100.00	100.00
	10^{-2}	100.00	100.00
	10^{-1}	100.00	100.00
6	10^{-3}	100.00	100.00
	10^{-2}	100.00	100.00
	10^{-1}	100.00	95.43
8	10^{-3}	100.00	100.00
	10^{-2}	100.00	100.00
	10^{-1}	100.00	100.00

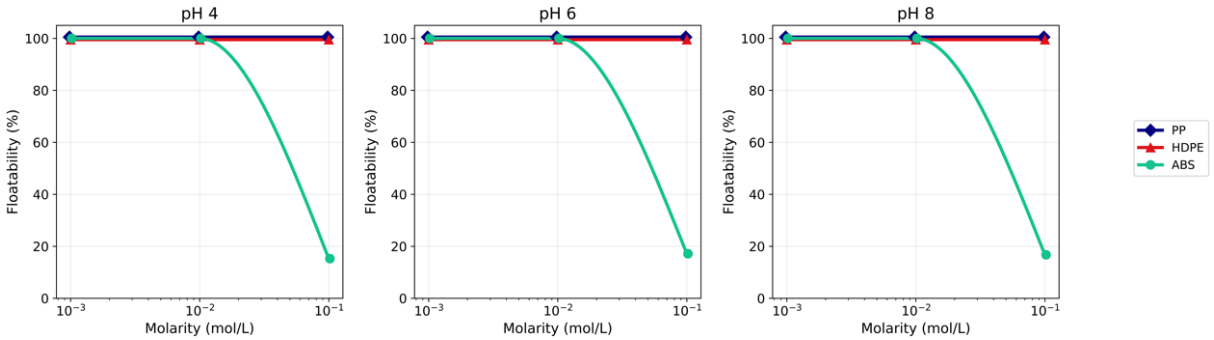


Fig. 13. Effect of DIB on virgin plastics floatability at different pH levels

Table 7. Micro-flotation results of LA at different pH levels

pH	Molarity (mol/dm³)	PP Floatability (%)	HDPE Floatability (%)
4	10^{-3}	100.00	93.68
	10^{-2}	20.24	0.00
	10^{-1}	17.15	0.00
6	10^{-3}	100.00	89.20
	10^{-2}	73.83	35.57
	10^{-1}	73.50	15.38
8	10^{-3}	100.00	100.00
	10^{-2}	100.00	90.73
	10^{-1}	100.00	90.26

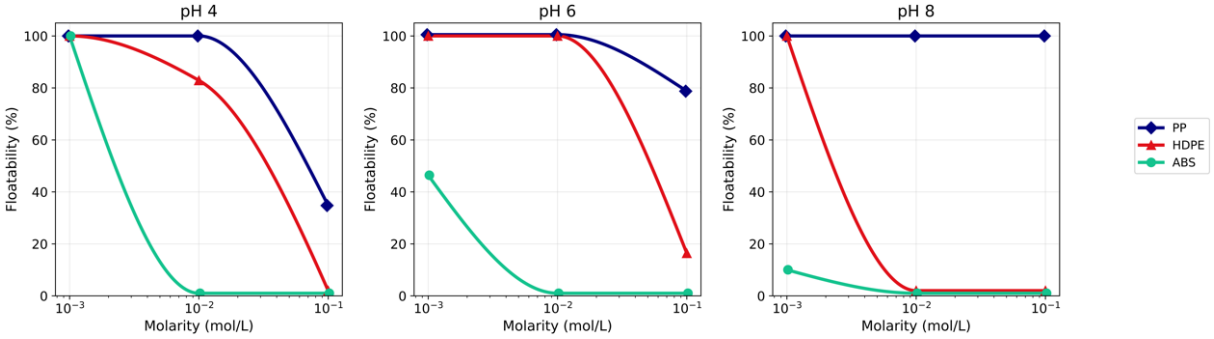


Fig. 14. Effect of LA on virgin plastics floatability at different pH levels

Fig. 14 illustrates the flotation behavior of PP and HDPE as a function of pH and LA concentration. At the lowest LA concentration (10^{-3} mol/dm^3), both polymers exhibited high floatability under all investigated pH conditions. However, increasing the LA concentration had a pronounced effect under acidic conditions. At pH 4, the floatability of both PP and HDPE decreased sharply as LA concentration increased. A similar trend was observed at pH 6, although the reduction was less severe than that observed at pH 4. In contrast, both polymers maintained relatively high flotation recoveries at pH 8 over the investigated concentration range.

These micro-flotation responses are highly compatible with the contact angle measurements. As demonstrated previously, increasing the LA concentration significantly lowered the contact angles, making the plastic surfaces highly hydrophilic. This increased hydrophilicity prevents air bubbles from attaching to the plastic particles, which directly explains the sharp decrease in floatability at higher LA concentrations. Therefore, the observed depression in micro-flotation is an expected and direct outcome of the surface modification confirmed by the contact angle results.

Overall, the graphs indicate that the flotation responses of PP and HDPE were similarly affected by increasing LA concentration. Consequently, LA failed to establish a sufficient difference in floatability between PP and HDPE to enable their selective separation under the investigated conditions.

Their chemical structures and interaction mechanisms can explain the distinct interfacial behaviors of DIB and LA with the plastic surfaces. DIB has very low aqueous solubility and lacks strongly hydrophilic or ionic groups. As a result, DIB molecules have limited interfacial activity and cannot readily form a stable hydrophilic layer on polyolefin substrates. Consequently, DIB induces only minor reductions in surface tension and contact angle, leaving both PP and HDPE predominantly hydrophobic across the investigated pH conditions. In contrast, LA exhibits an amphiphilic character containing both hydrophobic aromatic backbones and hydrophilic functional groups, such as hydroxyl and sulfonate groups. Because virgin PP and HDPE are non-polar polyolefins consisting purely of saturated hydrocarbon chains, they lack specific functional sites for chemical bonding. Therefore, the hydrophobic segments of LA adsorb non-selectively onto both PP and HDPE surfaces via hydrophobic interactions. Upon adsorption, the hydrophilic functional groups of LA are oriented toward the aqueous phase, rendering both plastic surfaces hydrophilic simultaneously. Because this adsorption process does not distinguish between PP and HDPE, LA reduces the contact angle and floatability of both polymers, preventing selective flotation separation.

4. Conclusions

This study evaluated the flotation behavior of virgin polypropylene (PP) and high-density polyethylene (HDPE) using diethylene glycol dibenzoate (DIB) and lignin alkaline (LA) through surface tension, contact angle, and micro-flotation analyses. DIB produced only a slight reduction in surface tension (from 72.8 mN/m to 61 mN/m) and caused only minor changes in the contact angles of PP (70.39°) and HDPE (70.74°). In contrast, lignin alkaline exhibited stronger interfacial activity, reducing the surface tension to 41 mN/m and decreasing the contact angles of PP and HDPE to 8.04° and 8.69°, respectively. Despite these differences, neither reagent generated sufficient wettability contrast between PP and HDPE to achieve selective flotation separation.

The micro-flotation results were consistent with the surface characterization analyses. DIB produced consistently high floatability values for both PP and HDPE (95–100%) under all investigated pH conditions and reagent concentrations, indicating that it failed to generate sufficient differences in the flotation behavior of the two polymers. Although lignin alkaline showed a much stronger effect on floatability, reducing PP floatability to 17.15% and HDPE to 0% under certain conditions, its influence was not consistent across the investigated pH and concentration ranges. Consequently, neither reagent provided the differential flotation response required for the selective separation of virgin PP and HDPE.

These findings demonstrate that flotation separation requires a distinct wettability contrast between polymers rather than strong overall hydrophilization. While contact angles above ~70° resulted in near-complete floatability (>90–100%), reducing contact angles below 20° with LA suppressed flotation for both plastics simultaneously (down to 0–17%), preventing selective separation. In the present study, DIB produced only limited surface modification, whereas alkaline-modified lignin altered the wettability of both PP and HDPE similarly, preventing the development of the differential wettability

required for selective flotation. This behavior is fundamentally linked to the inherent molecular structures of the reagents. The strongly amphiphilic LA adsorbs via its hydrophobic framework while directing its highly polar sulfonate and hydroxyl groups outward to create a hydration layer, whereas the ester-based DIB lacks the necessary polar functional groups to achieve this effect. The combined evaluation of surface tension, contact angle, and micro-flotation behavior provides valuable insight into the mechanisms governing plastic flotation. Future studies should therefore focus on developing reagent systems that selectively interact with only one polyolefin surface, such as selective collectors, depressants, or combined reagent strategies, while maintaining environmentally sustainable flotation conditions.

Acknowledgments

This study was supported by the Scientific Research Projects Coordination Unit of Istanbul Technical University (ITU-BAP) under Project ID: 47160. I would like to acknowledge and thank Istanbul Technical University for its financial support provided throughout this research.

We would like to thank Filiz Plastik Metal San. Tic. A.Ş. and Polser Polimer for supplying virgin plastic sheets for conducting the contact angle experiments.

A part of the results reported in this paper were presented at XX Balkan Mineral Processing Congress BMPC 2026 entitled "A sustainable approach of flotation-based recycling of virgin and post-consumer multiple plastics with determination of their surface characteristics".

References

BOLTE, L., GERS-BARLAG, H., HEINSOHN, G. & DANIELS, R., 2024. *Migration of cosmetic components into polyolefins*. Advances in Polymer Technology, 1, 2680899.

BRIGHTON TECHNOLOGIES GROUP, 2023. *Critical surface tension and contact angle with water for various polymers*. Retrieved from https://www.accudynetest.com/polytable_03.html

BURAT, F., GÜNEY, A., & KANGAL, M.O., 2009. *Selective separation of virgin and post-consumer polymers (PET and PVC) by flotation method*. Waste Management, 29(6), 1807-1813.

DUTSCHK, V., CALVIMONTES, A. & STAMM, M., 2012. *Wetting dynamics of aqueous surfactant solutions on polymer surfaces*. Drops and Bubbles in Contact with Solid Surfaces (eds M. Ferrari, L. Liggieri, and R. Miller), CRC Press, Boca Raton, 71-92.

FRAUNHOLCZ, N., 2004. *Separation of waste plastics by froth flotation–A review, Part I*. Minerals Engineering, 17(2), 261-268.

GEYER, R., JAMBECK, J.R. & LAW, K.L., 2017. *Production, use, and fate of all plastics ever made*. Science Advances, 3(7), e1700782.

GÜNEY, A., ÖZDİLEK, C., KANGAL, M.O. & BURAT, F., 2015. *Flotation characterization of PET and PVC in the presence of different plasticizers*. Separation and Purification Technology, 151, 47-56.

HOPEWELL, J., DVORAK, R. & KOSIOR, E., 2009. *Plastics recycling: Challenges and opportunities*. Philosophical Transactions of the Royal Society B: Biological Sciences, 364(1526), 2115-2126.

KANGAL, M.O. & ÜÇERLER, Z., 2018. *Recycling of virgin and post-consumer polypropylene and high-density polyethylene*. International Polymer Processing, 33(2), 268-275.

KANGAL, M.O., 2010. *Selective flotation technique for separation of PET and HDPE used in drinking water bottles*. Miner. Process. Extr. Metall. Rev., 31, 214–223. DOI:10.1080/08827508.2010.483362

KARAAGAC, E., KOCH, T., & ARCHODOULAKİ, V.M., 2021. *Choosing an effective compatibilizer for a virgin HDPE rich-HDPE/PP model blend*. Polymers, 13(20), 3567.

KÖKKILIÇ, O., MOHAMMADI-JAM, S., CHU, P., MARION, C., YANG, Y. & WATERS, K.E., 2022. *Separation of plastic wastes using froth flotation–An overview*. Advances in Colloid and Interface Science, 308, 102769.

MILLS, N.J., GILCHRIST, A. & JENKINS, M., 2020. *Plastics: Microstructure, properties and applications*. Elsevier.

NAGY, M., SKVARLA, J. & SİSOL, M., 2011. *A possibility of using the flotation process to separate plastics*. Annals of the Faculty of Engineering Hunedoara, 9(3), 275.

The Organization for Economic Co-Operation and Development (OECD), 2022. *Global plastics outlook: Economic drivers, environmental impacts and policy options*. OECD Publishing. https://doi.org/10.1787/de747aef-en

PITA, F. & CASTILHO, A., 2020. *Separation of PET from other plastics by flotation combined with alkaline pretreatment*. Polímeros, 30, e2020026.

PLASTICS EUROPE, 2023. *Plastics – the facts 2023*. Plastics Europe Association.

PLASTICS EUROPE, 2026. *The Circular Economy for Plastics – A European Analysis 2026*. Plastics Europe Association, Brussels.

SHEN, H., FORSSBERG, E., & PUGH, R.J., 2002. *Selective flotation separation of plastics by chemical conditioning with methyl cellulose*. Resources, Conservation and Recycling, 35(4), 229-241.

SIGMA-ALDRICH. (n.d.). *Alkaline lignin: 370959*. Retrieved from https://www.sigmaaldrich.com/TR/en/product/aldrich/370959?srsltid=AfmBOorc5CNiuFA719c-xgpyqYvn7lpbnsDvA7nGM40o520E6CegPt2Z

SIGMA-ALDRICH. (n.d.). *Di(ethylene glycol) dibenzoate: 369365*. Retrieved from https://www.sigmaaldrich.com/TR/en/product/aldrich/369365?srsltid=AfmBOopcN4jFOekJJ2ezv-cShVkdrBb5UKBu-Svx8kSx2h3U0x9TOMgJ

SIGMA-ALDRICH. (n.d.). *Product specification: Alkaline Lignin (Product No. 370959)*. Retrieved from https://www.sigmaaldrich.com/

SIGMA-ALDRICH. (n.d.). *Product specification: Di(ethylene glycol) dibenzoate (Product No. 369365)*. Retrieved from https://www.sigmaaldrich.com/TR/en/sds/aldrich/369365?userType=anonymous

SRITAPUNYA, T., KITIYANAN, B., SCAMEHORN, J.F., GRADY, B.P., & CHAVADEJ, S., 2012. *Wetting of polymer surfaces by aqueous surfactant solutions*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 409, 30-41.

YENİAL, Ü., BURAT, F., YÜCE, A.E., GÜNEY, A., & KANGAL, M.O., 2013. *Separation of PET and PVC by flotation technique without using alkaline treatment*. Mineral Processing and Extractive Metallurgy Review, 34(6), 412-421.

YUCE, A.E., & KILIC, M., 2015. *Separation of PVC/PET mixture from plastic wastes using column flotation technique*. J Environ. Prot Ecol, 16, 705-715.

ZHANG, Y., JIANG, H., WANG, K., WANG, H., & WANG, C., 2020. *Green flotation of polyethylene terephthalate and polyvinyl chloride assisted by surface modification of selective $CaCO_3$ coating*. *Journal of Cleaner Production*, *242*, 118441.

WANG, K., ZHANG, Y., ZHONG, Y., LUO, M., DU, Y., WANG, L., & WANG, H. (2020). Flotation separation of polyethylene terephthalate from waste packaging plastics through ethylene glycol pretreatment assisted by sonication. Waste Management, 105, 309-316.