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Discrimination of Plastic Waste using Laser-induced Breakdown Spectroscopy-principal Component Analysis: Highlighting Molecular LIBS

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P A P E R   I N F O

A B S T R A C T

Growing plastic waste emission as a planetary threat urges the development of a rapid and efficient recycling process, especially during the classification process. Herein, we aimed to solve the problem by employing laser-induced breakdown spectroscopy (LIBS) in combination with principal component analysis (PCA) as means for automated plastic waste classification. Samples used in the study were plastic wastes derived from beverage, food, and stationery products of different brands. The Nd:YAG laser was shot to the sample surface without a pre-treatment and under an open-air system (laser energy= 54 mJ; time delay= 1-2 μs). The spectral profile of each plastic waste revealed the presence of metal components such as those indicated by Ca II 396.85 nm, Al I 395.92 nm, Mg I 383.83 nm, and Fe I 404.85 emission lines. Peak intensities of organic material-related emission lines (C I 247.86 nm, O II 777.32 nm, O I 844.48 nm, H I 666.22 nm, N II 818.83 nm, and N II 821.62 nm) were revealed fluctuating, suggesting that a mere LIBS spectral analysis could not discriminate the plastic waste. PCA analysis revealed that C_2 molecular band 490—520 nm had the most discriminative properties against polyethylene terephthalate (PET) and polypropylene (PP). The molecular band was generated differently between PET and PP because of their contrast thermal behavior. In conclusion, molecular LIBS-PCA could be used to distinguish PET and PP in a simple and rapid way.

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NOMENCLATURE

LIBS	Laser-induced breakdown spectroscopy	PC	Principal component
PCA	Principal component analysis	ICP-MS	Inductively coupled plasma-mass spectrometry
PET	Polyethylene terephthalate	ICP-OES	Inductively coupled plasma-atomic emission spectroscopy
PP	Polypropylene	ICCD	Intensified charge-coupled device
LDPE	Low density polyethylene	DDG	Digital delay generator

1. INTRODUCTION

Plastics are notorious solid waste that contribute to the increased risk of human health and climate change through '*chain reactions*' [1]. With the current state of plastic generation, plastic waste emission is predicted to reach 35.8-90.0 Mt [2]. This number exceeds the mitigation efforts [2], suggesting the need of efficient plastic waste management. Of which, recycling is

considered to play a key role in saving the world from plastic waste disaster [3, 4]. One of the examples of the recycled plastic use is in asphalt mixture [5, 6], which requires certain type of plastics to achieve optimum durability. Prior to recycling process, an important step needs carried out is classifying the plastic waste based on its type [3]. Moreover, plastic waste should be classified further based on the contents of impurities and contaminants [3]. With our experience in previous researches of analyzing organic [7-9] or inorganic materials [10-13], we believed laser-induced breakdown spectroscopy (LIBS) could be the right technology to be applied to discriminate the plastic waste.

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LIBS is a versatile tool utilizing spectroscopical analysis on laser-ablated sample for multiple kinds of samples [14, 15]. Unlike complex inductively coupled plasma-mass spectrometry or -atomic emission spectroscopy (ICP-MS or -OES), LIBS uses a simple set up where the analysis is directly carried out on the plasma generated after the ablation. Interestingly, LIBS is capable of analyzing all elements in a single run without requiring sample pre-treatment [14]. Moreover, due to its simplicity, LIBS could be coupled with a machine allowing the automation of plastic separation [16]. In the case of plastic waste management, LIBS itself has been studied for its utilization to analyze hazardous impurities in plastics [17, 18]. Several previous reports have even suggested the discriminative ability of LIBS against various types of plastics or polymers [19, 20].

For discriminating plastic waste using LIBS, some studies were coupled LIBS with other analytical methods such as machine learning [19] and chemometrics [21, 22]. Indeed the grouping of plastics could be conducted based on simple analysis on the spectral intensities [23]. However, the investigation was only carried out on pure plastics [23], hence could not be used for plastic wastes that contain different kinds of additives or contaminants. Herein, we offer a simple chemometric technique namely principal component analysis (PCA). The technique reduces the dimensionality of large data sets [24], which is useful for LIBS spectral data with wide wavelength range. The objective of our study was to investigate the feasibility of LIBS-PCA for plastic waste discrimination. As a novelty of our research, we analyzed the plastic waste acquired from different products and brands. Moreover, the emergence of molecular band in the LIBS spectra was elucidated, contributing to more insights towards molecular LIBS.

2. MATERIALS AND METHODS

2. 1. Materials and Study Design   All plastic wastes used in this study were collected around Universitas Syiah Kuala (Banda Aceh, Indonesia) in June 2021. Based on the label, the plastic wastes consisted of several plastic types, namely polyethylene terephthalate (PET), polypropylene (PP), low density polyethylene (LDPE), and Teflon which were produced and used by different industries. PET was produced by PT. Coca Cola Indonesia (Jakarta, Indonesia) and PT Reckitt Benckiser Indonesia (Jakarta, Indonesia), PP – Zhejiang Xiulong Packaging Materials Co., Ltd. (Jiaxing, China), PT. Unilever Indonesia (Jakarta, Indonesia), and Jenia (Tanggerang, Indonesia), LDPE – PT. Sinergi Inti Plastindo (Jakarta, Indonesia), and teflon – PT. Unilever Indonesia (Jakarta, Indonesia).

Labels in the packaging were checked for the main polymeric components (PET, PP, LDPE, and teflon). Types or percentages of the additives in the packaging were not known to the researchers. Samples were directly shot using Nd-YAG laser without any pretreatment in an open-air system, where spectral data were then analyzed to discriminate the plastic wastes based on their respective type. All laser analyses were performed in triplicate to ensure the spectral stability.

2. 2. LIBS Set Up and Experiment   A Q-switched Nd:YAG laser (Quanta-Ray, LAB 130-10, USA) was used for the study. The laser was operated at 1064 nm with 8-ns pulse width and 10-Hz pulse duration to generate an ablation and plasma on a sample surface. The laser energy was set constant at 54 mJ. Prior of reaching the sample surface, the beam was focused using a lens with 150-mm focal length. The signals from the plasma were captured using an optical fiber (numerical aperture=0.22), distanced 6 cm from a sample. The signals were sent to a spectrometer coupled with an intensified charge-coupled device (ICCD) camera (Andor iStar' intensified CCD 1,024 x 256 pixels, UK). To trigger the laser and ICCD camera, a digital delay generator (DDG 535, Stanford Research System, USA) was employed. The gate width was of the ICCD was made constant at 30 μs with variation of time delays (1, 1.5, and 2 μs). The spectra were produced by 10 shots accumulation.

2. 1. Data Analysis   Principal component analysis (PCA) was carried out on spectra produced with 2-μs time delay using OriginLab version 9.6.5.169 (Northampton, USA), where data were extracted into 2 components. Spectral widths were obtained from a peak analysis carried out on the same OriginLab with constant baseline setting.

3. RESULTS AND DISCUSSION

3. 1. LIBS Spectral Profiles of Plastic Waste
Firstly, we conducted a spectral analysis on the whole wavelength to observe the differences between sample with wavelength range of 200 to 900 nm. The data are presented in Figure 1, depicting LIBS spectral profile for PET (1-4), PP (1-3), LDPE, and Teflon. Except in PP 1 and LDPE, CN (0,0) 388.3 nm bands appear significant in all samples. Discussion on CN band in details would be provided in the later part of this manuscript. Other than organic materials-related emission lines (C, H, O, and N), several metals could be observed in the spectra. Of which, Ca II 396.85 nm line is the most commonly appear. Interestingly, the emission line was significantly resolved at later delay time, assigned to the disappearance of ionic species in

the plasma [25]. Furthermore, Al I 395.92 nm and Mg I 383.83 nm emission lines are also present in several samples. Those metals could be associated to the presence of additives in the plastic packaging. Ca, in a form of $CaCO_3$, is the most popular additives in plastic [26, 27]. Al and Mg, or their combination (Al-Mg), are also added by the plastic producer to improve the material resistance [28]. It is worth mentioning that LDPE sample in this study had crowded spectral profile. Moreover, Fe I 404.85 line was uniquely found in the LDPE. There are reports where Fe, in its salt form, is added to the plastic matrix to produce more durable composite. These metals were also found in plastics waste from other countries [20].

Plastics, like other organic materials, mostly consist of carbon (C) and followed by hydrogen (H) and oxygen (O) [9, 29]. Hence, we present the data of C I 247.86 nm emission line of all collected samples in Figure 2. The spectral line could be observed even after the 2-μs time delay. In the spectrum of PET 4, the Mg II 280.23 line was attenuated significantly at later delay time, suggesting its decaying from the plasma. Though at longer delay time the atomic emission has a tendency to decay, several peaks were observed higher [30]. This is probably due to the discrimination between the emission line and continuum noise.

CN bands are common in carbon-containing material, especially when the ablation is carried out in an open-air [9, 12]. To observe the CN bands, LIBS spectra of each plastic waste focusing on the wavelength range between 300 nm and 400 nm are presented (Figure 3). The CN molecules could be deriving from the ablated C atom from the material and recombined with N from the material or from the ambient air [29]. Increase of CN band intensity is dependent on the delay time, ascribing to its formation during plasma cool down [31].
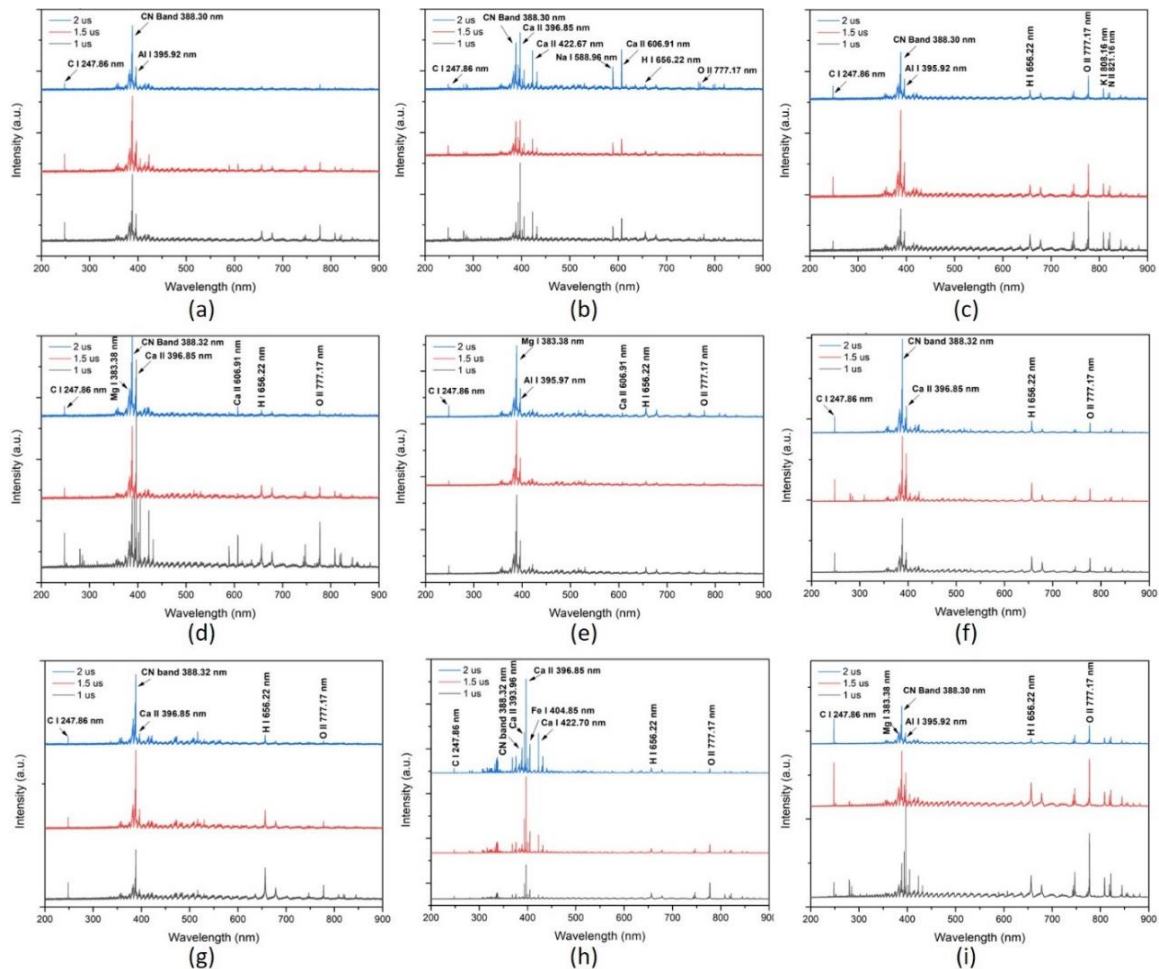

Figure 1. LIBS spectra of PET 1 (a), PET 2 (b), PET 3 (c), PET 4 (d), PP 1 (e), PP 2 (f), PP 3 (g), LDPE (h), and Teflon (i). Observed with delay time variation (1, 1.5, and 2 μs) at full wavelength (200—900 nm)
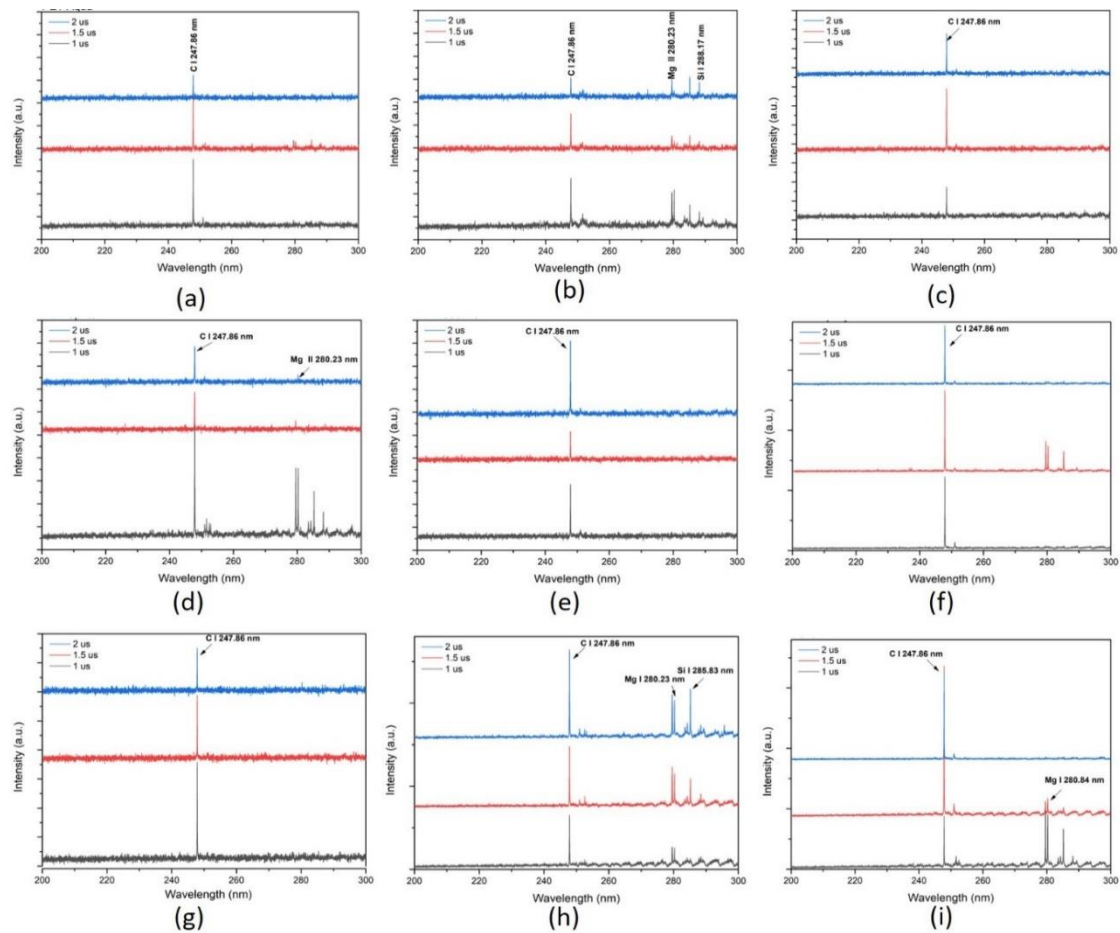
Figure 2. LIBS spectra of PET 1 (a), PET 2 (b), PET 3 (c), PET 4 (d), PP 1 (e), PP 2 (f), PP 3 (g), LDPE (h), and Teflon (i). Observed with delay time variation (1, 1.5, and 2 μs) at 200—300 nm

Within the wavelength range of 300—400 nm, several emission lines of metallic elements could be observed such as Mg I 383.32 nm, Al 394.75 nm, Al 395.92 nm, Ca II 393.36 nm, and Ca II 396.85 nm. Uniquely, multiple emission lines corresponding to Ti was present in LIBS spectra of LDPE. The presence of Ti in the plastic could be derived from TiO_2, a common coloring additive in plastics [32]. The presence of these metal could be an indication of plastic recyclability, where the presence of impurities might lower the quality grade of the recycled plastic [3].

O is also an interesting atom to be analyzed when it comes to organic sample. LIBS spectra ranged from 750 to 900 nm of all samples are presented in Figure 4, where typical emission lines for oxygen (O II 777.32 nm and O I 844.48 nm) could be observed. Except in PET 2, those aforementioned lines could be seen clearly even after 2 μs delay. In PET 2, the emission of O II 777.32 nm and O I 844.48 nm could be observed clearly only when the delay time was set at 1 μs, where their intensities reduced over time. Similar to carbon, oxygen

is also a light atom, capable of escaping the plasma during the early time of plasma generation [33]. Our data show interesting fact, despite its absence in several samples (PP, LDPE, and teflon), the presence of oxygen was captured in all spectra. It suggests that the oxygen is deriving from the ambient air, since its presence occupies around 21% of the total air; second most dominant after nitrogen (78%).

In this study, the presence of hazardous metals such as Pb, Cr or Hg was not found in the all plastics waste. Previously, LIBS was reported capable of identifying those aforementioned toxic elements in PP mixture [18]. Our suspicion regarding the toxic elements is based on the fact that heavy metals could form a surface chemical interaction with the binding sites available on the plastic [34, 35]. Therefore, even though the manufacturer does not add toxic metals to the plastic, it still capable of adsorbing the heavy metal from the environment. Based on these facts, plastics waste investigated herein are safe because of the absence of toxic heavy metals either originating from the producer or environment.
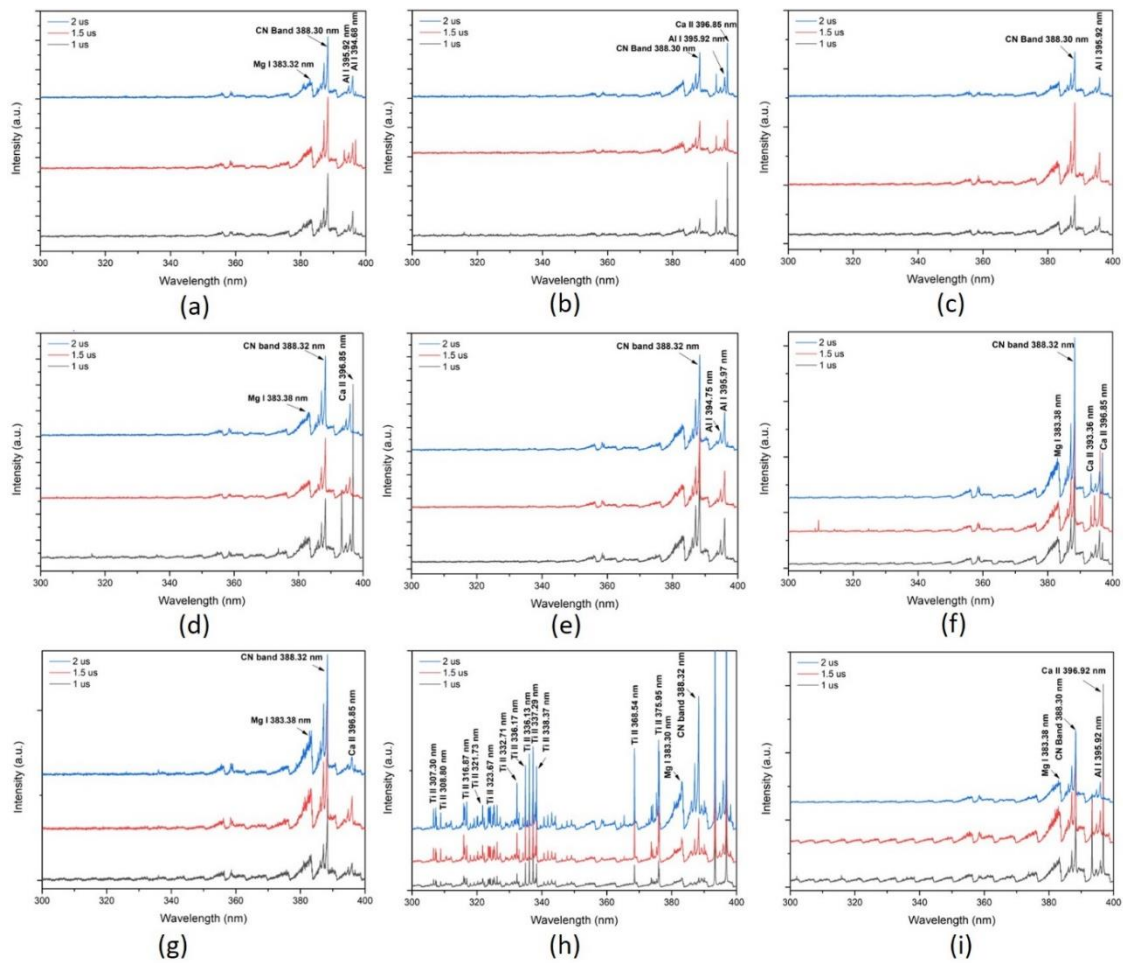
Figure 3. LIBS spectra of PET 1 (a), PET 2 (b), PET 3 (c), PET 4 (d), PP 1 (e), PP 2 (f), PP 3 (g), LDPE (h), and Teflon (i). Observed with delay time variation (1, 1.5, and 2 µs) at 300—400 nm.

Taken together, the spectral profile of each sample shows a variety of element components depending on the additives used by the producer. Even when we eliminate the mineral spectral lines and focus only to the organic spectral lines, the variation could be found. Not necessarily because of the open-air set up, but also because of the mineral additives are used as salts which commonly contains O and C (such as $CaCO_3$ or TiO_2). These differences suggest that LIBS could be used to inspect the origin of the plastic waste (brand or product). In regard of plastic waste management, we do not only expect to differentiate, but also to group the plastic based on its type. Therefore, in the following analysis, we wish to reveal the ability of LIBS to discriminate the plastic waste based on its type. To do that, we employed the data from PET and PP since their availability is more than 1.

3. 2. Discrimination of PET and PP Plastic Waste
To understand the underlying differences between PET

and PP, we have provided their chemical structure in Figure 5. PET has a cyclic carbon with ester, carboxylate, and alcohol functional groups. Meanwhile, PP has an aliphatic structure, with repeating C-C and one primary alkyl present along its chain. One may suspect that the presence of O in its structure could be the key in differentiating it with PP. Nonetheless, when it comes to commercial packaging O could also be found in PP deriving from the additives, as discussed previously. We ourselves have conducted the principal component analysis for LIBS spectra with wavelength ranges of 200—300, 300—400, and 750—900 nm. However, the analysis could not discriminate PET from PP (data not displayed).

To continue our efforts of discriminating PET from PP using LIBS-PCA, we focused on the C_2 molecular band at 464—474 nm (Figure 6a) and 490—520 nm (Figure 6b). It could be seen that the PP has higher intensities of C_2 molecular bands than that of PET in both observed wavelength ranges. Nonetheless, it is
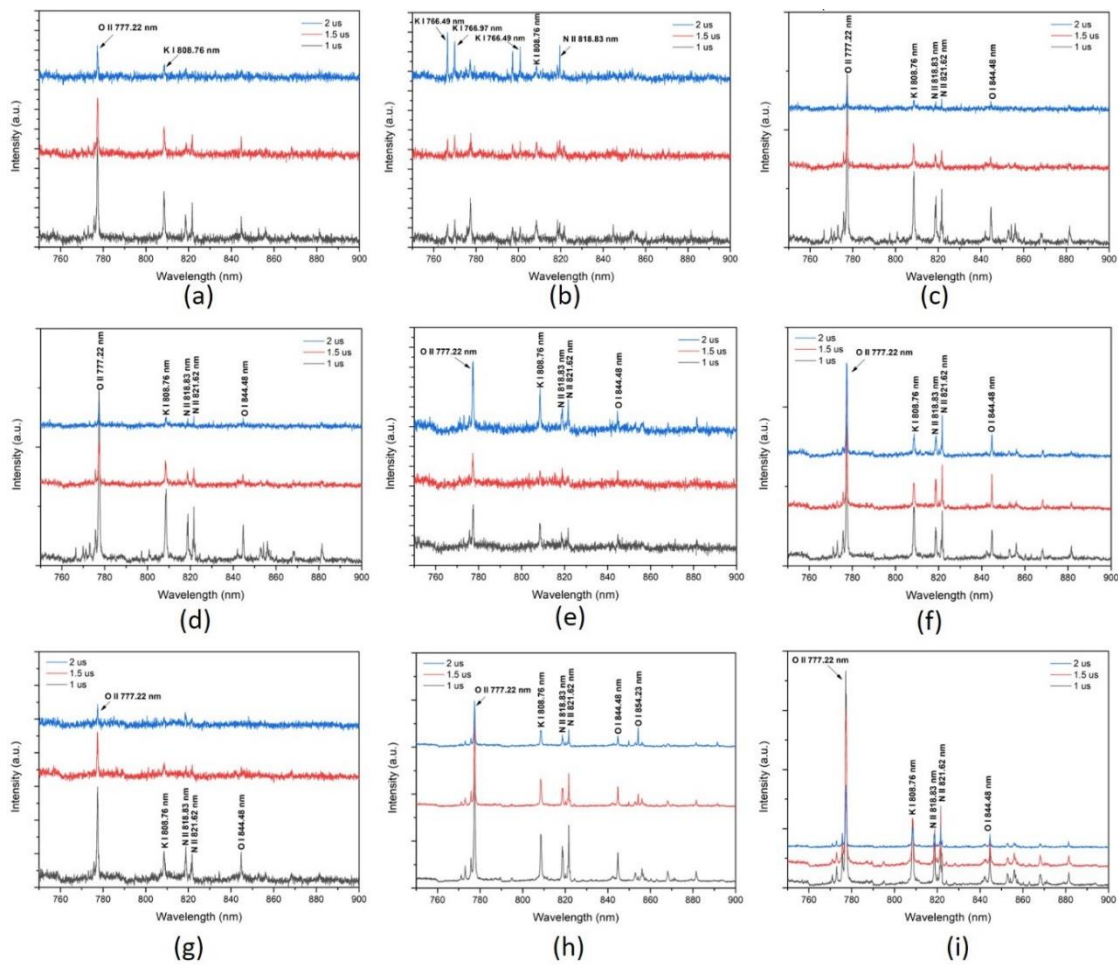
Figure 4. LIBS spectra of PET 1 (a), PET 2 (b), PET 3 (c), PET 4 (d), PP 1 (e), PP 2 (f), PP 3 (g), LDPE (h), and Teflon (i). Observed with delay time variation (1, 1.5, and 2 μs) at 750—900 nm.
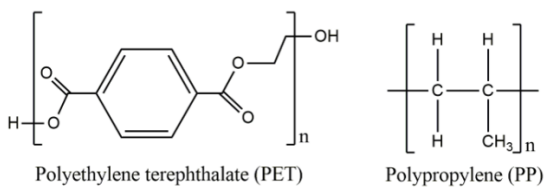

Figure 5. Chemical structures of PET and PP

impossible to discriminate the plastic waste based on this slight difference with human naked-eye. The PCA analysis using such wavelength ranges yielded satisfying results, where the data are presented in Figures 6b and 6c. It could be seen that the PET and PP could form their own group in the PCA plots. However, PET group at C_2 band at 464—474 nm is overlapping with that of PP. By observing the C_2 band at other wavelength range, the plastic waste could be grouped without overlapping one another (Figure 6d). Several studies have reported that the C_2 band at the range of

490—520 nm appears stronger than that of at other ranges [36, 37]. Taken altogether, C_2 molecular band at 490—520 nm could be used to distinguish PET from PP in an open-air system. In this study, there is no data pre-processing (such as smoothing) and only spectral data from wavelength range of 490—520 nm used. In comparison with other studies [38], this is a novel approach of employing LIBS-PCA that allows shorter time to complete the data processing due to less numbers of step and data used.

Correlation analysis using a combined data from PET (1-4) and PP (1-3) was shown to exhibit a positive correlation. Where increasing C I 247.8 nm spectral area could contribute to higher spectral area of the C_2 molecular band (Figure 7a). The Pearson's correlation coefficient (r) was obtained 0.862 with slope statistically significant than 0 according to ANOVA ($p < 0.05$). The emission from C atoms contribute to the formation of the molecular band of C_2 as high as 74.34%. Hence, ablation of carbon from the material
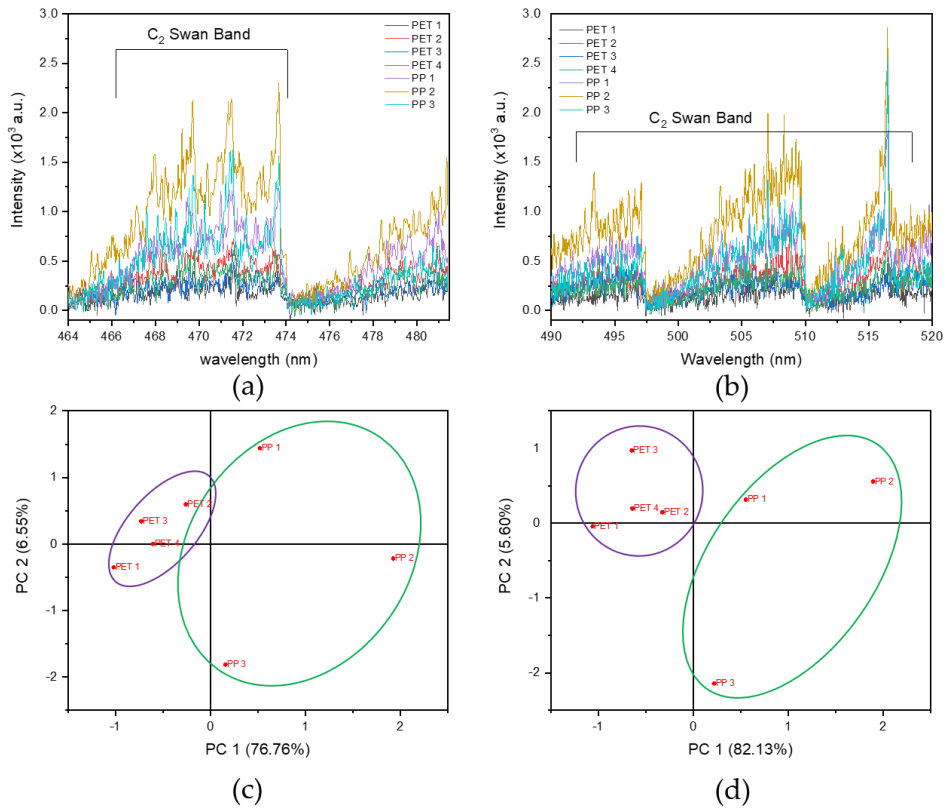
Figure 6. LIBS C_2 molecular band of PET (1-4) and PP (1-3), observed at 464—483 nm (a) and 490—520 nm (b). PCA plots obtained from LIBS spectra with wavelength ranges of 464—483 nm (c) and 490—520 nm (d). PC represents principal component.
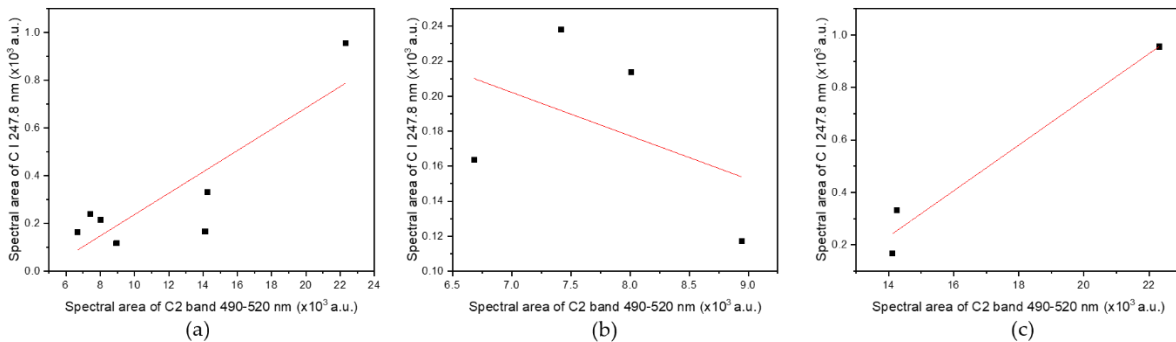

Figure 7. Linear correlation between the spectral area of C I 247.8 nm and spectral area of C_2 band 490-520 nm.

persists as the underlying factor that is responsible for the discrimination between PET and PP.

When further analyzed using the data from each plastic type, the correlation was obtained poor for PET (Figure 7b), where negative r value is negative (r = -0.441) and correlation percentage is small (19%). On contrary, spectral data from PP generated a better correlation with r value and correlation percentage

reaching 0.982 and 96.6%, respectively. It could mean that each type of plastic may have different origins of its molecular band in the LIBS spectra. Herein, the molecular band of C_2 captured in the LIBS spectra of PET could not be explained by the recombination of atomized C. We suspect that the C_2 molecules occupying the plasma are originated from the existing C—C bound.

Previous reports suggest that PET had better thermal stability than PP [39, 40], where thermal degradation of PET involved several binding cleavages [40]. In contrast, PP could be thermally degraded in a single step [39]. C_2 molecular band in the PET spectra possibly related to the thermal phenomena, allowing the C—C species to occupy the plasma. Consequently, the molecular band of C_2 in PET sample could not be explained solely by the ablated C variable. Nonetheless, to reach a better conclusion, more samples are required for the analysis

4. CONCLUSIONS

Plastics obtained from different products or brands have distinctive spectral profile, depending on the additives incorporated in the plastic. Thus, a mere spectral analysis LIBS is only capable of differentiating the plastic according to its producers. To discriminate the plastic wastes based on their types or chemical structures, employing the molecular band spectra was found to be strategic. Herein, we had successfully discriminated the PET and PP plastic wastes through PCA analysis on the spectral wavelength range of C_2 molecular band. The molecular bands of PET and PP were speculated to be dependent on the thermal degradation mechanism of PET and PP, which could be associated to their structure differences. Further investigation with higher number of samples and more plastic types is warranted.

5. FUNDING

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Persian Abstract

چکیده

انتشار زباله های پلاستیکی در حال رشد به عنوان یک تهدید سیاره ای، توسعه یک فرآیند بازیافت سریع و کارآمد، به ویژه در طول فرآیند طبقه بندی را ضروری می کند. در اینجا، هدف ما حل مشکل با استفاده از طیف‌سنجی شکست ناشی از لیزر (LIBS) در ترکیب با تجزیه و تحلیل اجزای اصلی (PCA) به عنوان ابزاری برای طبقه‌بندی خودکار زباله‌های پلاستیکی است. نمونه های مورد استفاده در این تحقیق، ضایعات پلاستیکی مشتق شده از محصولات نوشیدنی، مواد غذایی و لوازم التحریر با برندهای مختلف بود. لیزر Nd:YAG بدون پیش تیمار و تحت یک سیستم هوای آزاد به سطح نمونه شلیک شد (انرژی لیزر = ٥٤ mJ؛ تاخیر زمانی = ٢-١ میکرو ثانیه). مشخصات طیفی هر زباله پلاستیکی وجود اجزای فلزی مانند مواردی که توسط خطوط انتشار Ca II 396.85 نانومتر، Al I 395.92 نانومتر، Mg I 383.83 نانومتر، و Fe I 404.85 نشان داده شده است را نشان داد. اوج شدت خطوط انتشار مرتبط با مواد آلی (C I 247.86 نانومتر، O II 777.32 نانومتر، O I 844.48 نانومتر، H I 666.22 نانومتر، N II 818.83 نانومتر، و N II 821.62 نانومتر نشان می‌دهد که می‌تواند nm 821.62 را نشان دهد) برای زباله های پلاستیکی تبعیض قائل نشوید. تجزیه و تحلیل PCA نشان داد که باند مولکولی C2 490-520 نانومتر دارای بیشترین خواص متمایزکننده در برابر پلی اتیلن ترفتالات (PET) و پلی پروپیلن (PP) است. نوار مولکولی به دلیل رفتار حرارتی کنتراست آنها بین PET و PP متفاوت ایجاد شد. در نتیجه، LIBS-PCA مولکولی می تواند برای تشخیص PET و PP به روشی ساده و سریع استفاده شود.