Differentiation and Identification of Polymers using Laser-Induced Breakdown Spectroscopy (LIBS) in Combination with Multivariate Analysis Techniques

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Abstract

In recent years, the need for better sorting techniques has made it necessary for new methods of polymer identification and sorting to be developed. Laser-induced breakdown spectroscopy (LIBS) has received a lot of recognition for its potential applications in polymer identification, since it allows for fast analysis without sample preparation. In this study, LIBS, in combination with Principal Component Analysis (PCA) and k-means algorithms were used to distinguish between seven different polymers in a non-controlled environment: polycaprolactone (PCL), thermoplastic polyurethane (TPU), polycarbonate (PC), acrylonitrile styrene acrylate (ASA), polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and glycol-modified polyethylene terephthalate (PETG). The Adjusted Rand Index (ARI) and cluster variability (CV) were calculated and used in order to optimize the LIBS parameters delay time and laser power. The interquartile range (IQR) rule was used to identify and remove outliers for a more effective and reliable differentiation. Achieving a good repeatability of results was found to be challenging since this analysis heavily relies on external parameters. Nonetheless, the results obtained show that LIBS is a promising technique for polymer sorting.

Keywords: LIBS, Polymer Waste Sorting, Nanosecond Laser, Plasma, Atomic Spectra, Principal Component Analysis, K-means Clustering Algorithm

1. Introduction

Every year, hundreds of millions of tonnes of polymer waste are being produced, mostly from nonbiodegradable fossil hydrocarbons. These polymers can only be eliminated by thermal techniques, such as combustion or pyrolysis [1, 2].

Traditional waste management methods like these raise pollution and cause health concerns. In order to minimize these concerns, the polymers need to be sorted and reprocessed [3]. For decades, the only option was to sort the waste manually. With the rise of techniques such as near infrared (NIR) spectroscopy, automatization became possible. NIR spectroscopy has the advantage of low associated costs and a high accuracy, but it is unable to identify dark polymers.

Laser-induced breakdown spectroscopy (LIBS) is able to solve these problems. With a measurement only taking micro- to milliseconds, it is a suitable tool for a rapid analysis of materials. Furthermore, it does not require sample preparation. During LIBS, a pulsed laser creates a plasma on the sample surface by ablating and exciting a portion of the sample material [4, 5]. The plasma is an ionized gas with atoms, ions, molecules and free electrons that has no overall charge. A single laser pulse can initiate a plasma. At first, high ionization occurs, whereafter electron-ion recombination takes place, forming atoms and eventually molecules. During this process, a background continuum and spectral lines are emitted. The continuum decays faster, allowing the spectral lines to be analyzed. For this reason, a delay time t_d between the initiation of the laser pulse and the recording of the signal is set. The atoms and ions of an optically thin plasma will emit line radiation, resulting in a complex spectrum containing information about the elemental composition of the ablated material. Like this, it is possible to distinguish different materials [4, 6]. The lifetime of the plasma depends on the laser parameters, the surrounding atmosphere and the sample, and ranges from 0.5 μ s to 10 μ s [7].

Developing a reliable strategy for the discrimination of polymers using LIBS is no simple task, as one of the limitations of using LIBS in polymers is the similarity between spectra. Furthermore, LIBS depends on different complex interactions between the laser, the sample and the environment [8]. Varying physical properties of the sample matrix, such as the melting point, or the density, can influence the spectral results. This is called the physical matrix effect. The chemical matrix effect describes the influence of inhomogeneities in the chemical composition of the sample matrix [9]. The spectral results can be influenced by noise. The main types of noise that have to be taken into account are the detector noise, the source noise and the shot noise. Source noise is composed of the influence of the fluctuations in the laser-sample and laser-plasma interactions, as well as the noise resulting from the drift in the optical focusing and collecting system which occurs at high temperatures. The shot noise depends on the variation in the number of photons arriving at the detector during a measurement [10]. As the plasma interacts with the atmosphere, the atmospheric pressure is an important parameter to take into consideration. With decreasing pressure, the intensity of the obtained spectra decreases as well, while the signal-to-noise ratio increases [11].

Different statistical methods, such as artificial neural networks or supported vector machines, are commonly used to identify polymers from spectral data obtained through LIBS. In this paper, principle component analysis (PCA), a tool for the reduction of dimensionality of a data set in order to recognize patterns, and the k-means clustering algorithm, were used to evaluate the obtained spectra [4, 12].

2. Methodology

2.1 Experimental

2.1.1 Sample preparation

The polymers investigated in this paper were polycaprolactone (PCL), thermoplastic polyurethane (TPU), polycarbonate (PC), acrylonitrile styrene acrylate (ASA), polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and glycol-modified polyethylene terephthalate (PETG). Their structural formulas can be seen in Table I. A part of the samples was chemically produced, while the rest was 3D printed and provided by the department of Materials and Production of Aalborg University. For the production of the PCL samples, raw material in form of a powder was used. It was heated on a metal plate that was functioning as a mold. This mold was heated up on a heating plate at 100°C, so that it could be guaranteed that the PCL was heated up to its melting point of 60°C. The PC samples were produced through evaporation. A dissolution of PC in dichloromethane (DCM) of approximately 15% was prepared. It was then poured into a mold of a suitable diameter, such that the sample was ensured to fit on the sample stage. The DCM evaporated over time, resulting in samples of pure solid PC. The PLA, PETG, TPU, ASA and ABS samples were produced with a 3D printer.

2.1.2 Experimental set-up

A 5 ns pulsed Nd:YAG laser (Continuum Surelite II-10) operating at a repetition rate of 10 Hz and a wavelength of 1064 nm was used to create the LIBS plasma. The emitted plasma light was then collected and measured using a AvaSpec2048CL-RS-EVO spectrometer with a diffraction grating covering the range between 300 nm and 815 nm.

A schematic representation of the experimental set up can be seen in Figure 1. An RG850 light filter in front of the shutter was used to remove wavelengths below 850 nm. A dielectric mirror directed the beam to the sample stage. To focus the beam onto the sample, a DCX 200 mm lens was employed. A fused silica 50 mm focal lens was then placed to focus the light emitted by the plasma onto an optical fiber. A KG3 filter was placed to filter out the infrared light, preventing damages to the optical fiber, which transmitted the light to the spectrometer. In order to achieve a more homogeneous ablation, the sample stage was rotated using a connected motor. To be able to set a delay time between laser pulses and signal collection, the laser output trigger signal had to be inverted before reaching the spectrometer.



Fig. 1 Scheme of the experimental set up.



Tab. I Polymers used in this work and their respective chemical structures.

2.2 Data analysis

The raw spectra need to be processed so that the relevant chemical information needed to identify each polymer can be extracted. For that, the data was imported to MATLAB, where this information was obtained in the form of spectral descriptors. These represent properties of specific regions of each spectrum, such as peak intensities or areas, selected in regions that differ from polymer to polymer. In this study, the chosen regions were the ones comprising the cyanide (-CN), hydrogen (H) and oxygen (O) peaks, as seen in Table II.

Tab. II Emission signals and corresponding wavelength ranges for the chosen set of spectral descriptors.

Emission signal	Wavelength range (nm)
CN violet band	380 - 390
H (I)	650 - 660
O (I)	775 - 780

Inspired by previous work on polymer differentiation [4], three descriptors were chosen for each peak: the area under the curve with baseline subtraction, its maximum intensity subtracting the baseline and its maximum intensity without baseline subtraction. These can be seen represented in Figure 2. As these descriptors were calculated for the three peaks, a total of nine descriptors were used.

Before analysing them, the raw spectra were preprocessed by background removal. A reference *dark* spectrum taken for each set of measurements was subtracted from the virgin polymer spectra. This dark spectrum contained the data obtained previous to the plasma formation. Next, the descriptors information was extracted, indexed in matrix form and standardized. Standardization of descriptors was carried out by setting the mean for each measurement to zero and the standard deviation to one.



Fig. 2 Types of spectral descriptors used in this study. Maximum intensity with baseline subtraction (left), maximum intensity without baseline subtraction (middle), and area under the curve with baseline subtraction (right). These are calculated for the CN, H (I) and O (I) peaks for a total of 9 descriptors.

The standardized matrix was then used as an argument for the k-means clustering function, which placed the different values into k different clusters. However, these clusters were nine dimensional, accounting for the nine descriptors. For that reason, multivariate analysis - principal component analysis (PCA) - was carried out using a predefined MATLAB algorithm. In that way, dimensionality was reduced from nine to two dimensions.

These k-means/PCA results, however, can contain values considered extreme and too different from all other data. These values, outliers, were removed by the interquartile range (IQR) method. Points either below the lower limit of the 25th percentile of the data or above the upper limit of the 75th percentile were discarded in this last step.

3. Results

3.1 Optimization of LIBS parameters

In order to optimise the setup parameters for the LIBS analysis, several evaluation tools were needed. The cluster purity and the variability within each cluster were the parameters chosen to quantify the quality of the obtained results for four of the polymers (PCL, PC, PLA, TPU). For this analysis, five measurements of each polymer sample were taken.

To measure cluster purity, the Adjusted Rand Index (ARI) was used. The ARI was calculated from a contingency table, similar to Table III, where $U = \{u_1, u_2, \ldots, u_R\}$ refers to the different clusters and $V = \{v_1, v_2, \ldots, v_C\}$ refers to the different polymers (e.g: v_1 =PLA). n_{ij} represents the number of measurements allocated in cluster j being polymer i.

Tab. III Contingency table notation.

	v_1	v_2	 v_C	Sums
u_1	n_{11}	n_{12}	 n_{1C}	$n_{1.}$
u_2	n_{21}	n_{22}	 n_{2C}	$n_{2.}$
•	•	•	•	
u_R	n_{R1}	n_{R2}	 n_{RC}	$n_{R.}$
Sums	$n_{.1}$	$n_{.2}$	 $n_{.C}$	$n_{} = n$

With the contingency table, it was possible to apply the adjusted Rand Index mathematical expression, expressed in Equation (1), where $\binom{n}{2} = \frac{n(n-1)}{2}$.

$$ARI = \frac{\sum_{i,j} \binom{n_{ij}}{2} - \left[\sum_{i} \binom{n_{i.j}}{2} \sum_{j} \binom{n_{.j}}{2}\right] / \binom{n}{2}}{\frac{1}{2} \left[\sum_{i} \binom{n_{.j}}{2} + \sum_{j} \binom{n_{.j}}{2}\right] - \left[\sum_{i} \binom{n_{.j}}{2} \sum_{j} \binom{n_{.j}}{2}\right] / \binom{n}{2}} \quad (1)$$

The Adjusted Rand index value lies between 0 and 1. Its value will be 1 when all measurements for samples of the same polymer are allocated in the same cluster. However, it will be very low, close to 0, if the data is randomly distributed and has no clustering tendency.

The other method used to evaluate the quality of the results was the variability within each cluster. This value is calculated, for each cluster, as the mean of the point to centroid euclidean distance. The value considered for the optimisation, cluster variability (CV), is the sum of this mean for every cluster.

3.1.1 Laser Power

The laser power is one of the controllable settings in the setup, having a significant impact on the formed plasma. With the laser being the most expensive component of the setup, being able to use lower laser powers, would be beneficial as a more compact and affordable laser could be used. Nonetheless, it is necessary that the plasma created has good enough characteristics for a reliable analysis.

In order to analyze the relation between laser energy and the quality of the obtained spectra, a sweep of laser powers, from 65 mW to 610 mW was made. These values of average laser power translate into a range of laser energies per pulse from 6.5 mJ to 61 mJ. The power of the laser is directly related to the intensity of the spectra. Generally, higher power leads to higher intensity as shown in Figure 3, but also higher continuous background signal.



Fig. 3 Relation between intensity and laser power, in miliwatts, for 4 different polymers. The general tendency is for higher laser powers to lead to higher signal intensities.

Since the goal is to have the largest signal-to-noise ratio possible, it is necessary to compromise on lower intensities. A quality test was preformed to find which value of laser power would achieve the best results.

Using the ARI and the CV implemented in the MATLAB code, the effect of the laser pulse energies on the clustering can be studied so the best laser power is selected. The results obtained from such analysis are shown in Table IV. With these results, it is possible to see that the best energy to use is 13mJ per pulse, corresponding to 130 mW of average laser power, since it showed the best possible differentiation, which translates to an ARI value equal to one and the the lowest value for CV comparing to other powers with an ARI of one.

Laser Power (mW)	Energy _{pulse} (mJ)	ARI	CV
65	6.5	0.583	3.749
130	13	1	0.777
265	26.5	1	1.096
370	37	0.768	1.307
469	46	1	1.660
550	55	0.545	2.277
610	61	0.586	3.036

Tab. IV ARI and CV obtained for different laser powers.

3.1.2 Delay Time

The dependence of the obtained spectra on the delay time is considerable, as illustrated in Figure 4. Larger delay times lead to a decrease in the continuous part of the spectrum as well as in the total intensity, leading to the loss of some minor peaks. A small delay time leads to the presence of undesirable continuous background signal, which affects individual peak intensities. That being said, it is necessary to optimise the value for the delay time so that a compromise can be achieved.



Fig. 4 Influence of delay time in the obtained spectra. As delay time is increased, the continuous part of the spectrum decreases. However, the total intensity decreases as well.

In order to find the best delay time for this setup, different delay times were tested. The laser power for this experiment was set to 130 mW since it was previously found to deliver the best results. The delay times tested were 0, 0.250, 0.500, 0.750, 1, 1.5, 2, 2.5, and 3 μ s.

The quality of the results was evaluated with the same tools used for the laser power, ARI and CV, and the results are shown in Table V. The ideal results for this test would be to achieve an ARI value equal to one and the lowest CV possible, similar to what was done with the laser power.

Tab. V	V	ARI	and	CV	obtained	for	different	delay	times.
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Time Delay (μ s)	ARI	CV
0	1	0.838
0.25	0.845	0.706
0.5	1	0.851
0.75	0.820	1.067
1	1	0.777
1.5	0.835	1.094
2	1	1.392
2.5	1	1.528
3	0.587	1.307

From Table V it can be found that an ARI equal to one can be achieved for different delay times and that the biggest differences are related to the value for CV. It is clear that CV has an increasing tendency when the the delay time gets larger, as demonstrated in Figure 5. From 1.5 μ s to 3 μ s, all the respective CV values are above one, whereas for lower values of delay time it is seen that CV is around 0.80. From this, it can be assumed that the optimal delay time is below 1.5 μ s. Considering only the values below 1.5 μ s, for which the ARI value is one, it is observed that 1 μ s is the delay time with the lowest CV value. Therefore, it is chosen as the optimal delay time.



Fig. 5 Relation between CV and delay time. An increasing tendency of larger CV values for higher delay times can be observed.

4. Identification of polymers

As a first approach, the intensity ratios of the characteristic hydrogen and oxygen peaks in the spectra were evaluated. It showed that the repeatability was low and the influence of the environmental conditions and additives in the polymer samples was big. Therefore, additional descriptors needed to be added to evaluate the measured spectra. PCA and k-means algorithms were employed to identify the polymers instead.

Three new polymers were added to the batch of samples - ABS, ASA and PETG - in order to verify if the correct differentiation of a larger number of polymers, seven, was achievable. Using the optimised settings, the result present in Figure 6 was obtained.

The obtained PCA plot accounts for around 99% of the total data variance and has an ARI of one, i.e., each cluster has only one type of polymer present, so a successful differentiation of the seven polymers was achieved. PLA samples with nine different colors were also added to verify that the dyes that are added to achieve different colors would not have a strong influence on the clustering. All PLA samples are contained in the same cluster, indicating that the methodology applied is not strongly influenced by the sample colors. Although some variability is observed, it cannot be said with certainty that this is caused by the colors as the same amount of variability is present in other clusters. It is also clearly seen that some polymers measured have a higher variability than others This can become a problem when a higher number of polymers is analyzed, as the clustering of different polymers onto the same cluster would more easily happen, reducing the effectiveness of the method. The existence of outliers is also of great importance, as these will affect the results obtained significantly.



Fig. 6 PCA plot of the seven polymers: PCL, PC, TPU, PLA, PETG, ABS, ASA. A successful differentiation was achieved.

4.1 Outlier Removal

All results so far have been presented after the outlier removal process. To have a visual perception and understanding of why this step is important, Figure 7 represents the same data set utilized as for Figure 6 but without the outlier removal process. Comparing both results, the difference is clearly noticeable. The cluster process resulted in a different arrangement of the points, as points from the previous Clusters 3, 4 and 5 are now mixed. Circled in Figure 7 are the correct clusters for such points and represented as red triangles are the measurements identified as outliers. Of these four outliers, two of them seem to have a higher impact than the others, the one detected in Cluster 3 and the one from Cluster 4. Because of these two, the centroids calculated by the k-means are dislocated, influencing the clustering of all the other "non-outlier" measurements. In this example, because of the outliers, three out of seven clusters are wrongly clustered. The outlier detection and consequent removal is of major importance for the high effectiveness of the differentiation mechanism.



Fig. 7 PCA plot of seven different polymers without the outliers removed. Clusters 3,4 and 5 are a mix of polymers (TPU, PLA, PETG). The identified outliers are marked with red triangles.

For the outlier removal, the MATLAB code goes trough each cluster and uses the IQR rule for every descriptor in order to identify outliers. If any data point has at least one descriptor detected as an outlier, the measurement is removed. Figure 8 illustrates a boxplot, a visual way to display the IQR rule, for the PLA samples, using the Oxygen raw peak intensity descriptor. The blue box contains the middle quartiles and from the box edge to the upper or lower limit the upper and lower quartile are contained respectively. Any point outside the limited zone is considered an outlier. In this example, the point outside is the PLA outlier mentioned above. Even though only one boxplot is represented, when looking trough the boxplots for the other descriptors this measurement was identified as an outlier more times.



Fig. 8 Boxplot of the oxygen raw peak for PLA measurements. Inside the blue box are the middle quartiles and from the edge of the box until the upper or lower limit are the accepted points of the upper and lower quartiles respectively. Any point outside these limits are considered outliers. In this boxplot, one point is identified as such.

4.2 Repeatability

Figure 9 presents three different k-means/PCA analysis carried out with the same set of samples (PC, PC, PLA and TPU) in three different measuring sessions. In the bottom plot, a perfect clustering - ARI of one - can be seen, where PCL is Cluster 1, PC is Cluster 2, TPU is Cluster 3 and PLA is Cluster 4. In the middle one, the clustering was not perfect as one TPU measurement is wrongly clustered with the PLA ones. In the top plot, two PLA measurements are wrongly clustered with the TPU ones. Although not all measurements are sorted into the correct cluster, the clustering is still acceptable, proving the method to be promising.

One of the main issues faced during this study was the non-uniformity of results for different measuring sessions. While the distinction of different polymers was achieved when using measurements taken during the same session, when adding measurements from another session, these will not cluster correctly. The same sample, if measured in different times, has a different *fingerprint*, which makes the construction of a database for future differentiation challenging with the setup used in this study. Figure 9 illustrates the behaviour previously explained. Although the different PCA plots look very similar, a closer inspection of the Y-axis makes clear that the clusters are varying their coordinates from session to session.

The non-controlled environment may be one of the causes for this behavior, since the surrounding envi-

ronmental conditions, such as atmospheric pressure, change from session to session. Other factors that may be responsible for such deviations are the sensibility of the used spectrometer to misalignment, reflections due to the position of the sample on the sample stage, polymer decomposition and transparency of some samples, which allowed the laser light to be scattered and transmitted through them. This last factor is believed to cause the appearance of an aluminium peak in the spectral results, since it was what the sample stage is made of.



Fig. 9 PCA plots of PCL, PC, TPU and PLA samples from different measuring sessions. It can be observed that cluster positions change for each session.

5. Conclusions

In this paper, it has been proven for LIBS to be a reliable method for the differentiation and classification of polymers when coupled with multivariate analysis techniques. Firstly, the LIBS setup was optimized as to reach a compromise between spectra intensity and signal to background ratio. This analysis was carried out for both laser power and the delay time between each laser pulse and signal detection, employing Adjusted Rand Index (ARI) as a measure of cluster purity and calculating cluster variability (CV). Regarding laser power, 130 mW or an energy per pulse value of 13 mJ showed the best results. For delay time, the best results for these polymer sample set were obtained for 1 μ s. Then, k-means and principal component analysis (PCA) were used to differentiate 7 polymers, which was possible when coupled with the removal of outliers. This last step improved the accuracy of the 7 polymers differentiation to 100%. In addition, with the methodology used, the influence of color additives in the differentiation process was successfully surpassed.

However, repeatability was limited, as cluster positions change for different measuring sessions. This drawback might be caused by changing experimental conditions, such as small misalignments in the focusing of plasma light on the optical fiber or changes in atmospheric conditions.

For future work in polymer differentiation, a diffraction grating enabling a wavelength range that comprises the emission signal range for carbon - around 247 nm - and other common elements found in polymers, could be helpful in improving the multivariate analysis ability to distinguish more polymer types.

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