



Technical note

Plastic identification based on molecular and elemental information from laser induced breakdown spectra: a comparison of plasma conditions in view of efficient sorting



Sophie Barbier^a, Sébastien Perrier^a, Pierre Freyermuth^b, Didier Perrin^c, Benjamin Gallard^c, Nicole Gilon^{a,*}

^a Institut des Sciences Analytiques, UMR 5280, CNRS, Université de Lyon, Villeurbanne, France

^b EFS Technologies, Montagny, France

^c Centre des Matériaux de Grande Diffusion, Ecole des Mines d'Alès, Alès, France

ARTICLE INFO

Article history:

Received 23 July 2012

Accepted 21 June 2013

Available online 28 June 2013

Keywords:

LIBS

Polymer sorting

Element determination

Laser induced plasma conditions

ABSTRACT

This work is dedicated to a comparison of plasma conditions for the accurate determination of some elements: Br, Cl, Ca, P and Sb, in polymers. The comparison of the plasma conditions to sort plastics according to CN, C2 and element signals was also investigated. The comparison of a helium atmosphere and an air atmosphere led to improved results using helium as a buffer gas. The improvement is obtained in two areas, it increased the detection of halogens (Br, Cl) usually employed as flame retardants. It was also found to significantly improve the discrimination based on simple calculations of C2/He and CN/He ratios. Best conditions were based on a laser emitting at 266 nm, with a low 6 mJ energy focalized on a 50 μm spot and the helium buffer gas. A plot of C2/He against CN/He was efficient to identify the four groups of plastics employed in this study: polystyrene, polypropylene, acrylonitrile–butadiene–styrene and acrylonitrile–butadiene–styrene/polycarbonate.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The determination of the elemental composition of polymers and plastics is a topic of interest to improve waste management. Recycling consumer goods requires an efficient waste sorting to remove potentially toxic plastics from the recycling process, several strategies have been studied in the past decades [1,2]. The stage of sorting is performed mainly using vibrational spectroscopy including infrared and Raman spectroscopy. It is also a current issue of laser induced breakdown spectroscopy (LIBS). If LIBS remained long a technique strictly dedicated to the determination of the inorganic elements, some works deal now with the determination of organics employing the rich LIBS spectra [3–6].

Different emissions, including elementary and molecular information, are often combined to perform an efficient plastic sorting. Due to the particular composition of plastic additives [6], the detection of both flame retardants (Br, Cl ...) and toxic metals involved in pigments (Pb, Cd, Hg ...) is required. In addition, as the visible region of the spectrum is dominated by carbon and molecular emission, the identification of certain elements such as Zn or S is made through unusual low UV wavelength. Thus, Jasik [7] employed a laser-induced breakdown spectroscopy in the vacuum ultraviolet range (VUV, λ below 200 nm) for the detection of trace elements in polyethylene

(PE) that is difficult to detect in the UV/VIS range. For effective laser ablation of PE, they employed an excimer F₂ laser (wavelength $\lambda = 157$ nm) with a high pulse energy, of up to 50 mJ, they obtained a limit of detection (LOD) of 50 $\mu\text{g g}^{-1}$ for sulfur and 215 $\mu\text{g g}^{-1}$ for zinc, respectively, in polymer reference materials.

Bromine, used as a flame retardant in thermoplast is also one of the difficult-to-detect elements. A comparison of LIBS analytical criteria based on two Br lines: Br I 827.244 nm and Br I 130.991 nm, showed that the detection limit could be improved by a factor of three when using the low UV Br line [8]. To avoid oxygen, the sample is placed in an argon flushed cell and a vacuum monochromator is employed. An improved detection limit is also obtained using double pulse LIBS, this method was described for the detection of heavy metals (Cd, Hg, Pb) in the low 300–1100 $\mu\text{g g}^{-1}$ range [9].

With the benefit of rich spectral information, the need for discrimination between samples has also led to an abundant chemometric literature. The high amount of information provided by an LIBS spectra is efficiently simplified using Principal Component Analysis (PCA), it allows to classify plastics or to simply identify outliers [10]. Simple ratios determinations were also employed [6,11]. Independent Modeling of Class Analogy (SIMCA) was also compared to linear correlation and PCA to discriminate different organic samples [12]. A complete analysis of many plastics: polyethylene (PE), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET), was made using hierarchical cluster analysis, the mentioned polymers could then be classified into two clusters and were further separated [13]. Methods of normalized

* Corresponding author.

E-mail address: gilon@univ-lyon1.fr (N. Gilon).

coordinates, linear and rank correlation were applied to identify polymers with a very similar chemical composition [14]. Best results were obtained using the linear correlation method. To control the occurrence of toxic elements in toys, Discriminant analysis, Soft independent modeling and K-Nearest Neighbor (KNN) were also compared [15]. The classification models were established and eleven organic materials including: PS, PP, PET, HDPE, LDPE (high- and low density polyethylene), PVC (polyvinyl chloride), and PTFE (polytetrafluoroethylene) were studied. The KNN method gave the best results with a correct prediction of 95% for Cd occurrence in toy sample, and 100% for Cr and Pb [15,16]. The work of Boueri [17] demonstrates a successful treatment of LIBS spectra with neural network for the identification of PP, PVC, PE, PTFE, POM (polyoxymethylene), PA (polyamide or nylon), PC (polycarbonate) and PMMA (poly-methylmethacrylate). The identification rates were ranging between 81 and 100% [17]. Using a careful temporal signal optimization Gregoire [18] also compared different statistical treatments of polymer spectra: line ratios, PCA and PLS (Partial least square). The discrimination was possible, even between polyethylene and polypropylene using this protocol [18].

This work is dedicated to select criteria based on LIBS spectra for plastic sorting. A comparison of plasma conditions for the accurate determination of some elements present in polymers as well as the validity of molecular information for plastic nature identification was made. A comparison of elements response in the different polymers was established. The careful evaluation of fluence and buffer gas nature was also discussed in view of lowering the detection limits for chlorine and bromine flame retardants. The plasma conditions were also investigated to establish best conditions to use CN/He and C₂/He ratio intensities to efficiently discriminate plastics investigated in our work: polystyrene, polypropylene, acrylonitrile, 1,3-butadiene-styrene (ABS) and a mixture of ABS with polycarbonate.

2. Experimental

2.1. Materials

Tested reference plastics were containing five different additives into four thermoplastic polymers used for electrical and electronic applications in controlled concentrations. The nature of each polymer and concentration of the additives are presented in Table 1.

Commercial grade ABS (Terluran GP22), HiPS (Escrimo KG2), ABS-PC (C2800) and PP (3400MA1) polymers were purchased from BASF (ABS and HiPS), Sabic and Appryl respectively. In the following text these polymers will be referred as A for ABS, H for HiPS, C for ABS-PC and P for PP.

The commercial additives employed were calcium carbonate for calcium addition (Socal), chloride flame retardant as 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo[a,e]cyclooctene (Dechlorane C25 Plus),

phosphorus flame retardant as ammonium polyphosphate (Clariant AP423), bromide flame retardants as tetrabromobisphenol A (Aldrich) and as decabromodiphenylether in synergy with antimony oxide (FR1203). For each of the additives, four to five plastic pieces were available; these were containing increasing concentration of the additive from 1 to 20% w/w. For each of the concentrations, again four samples were available.

2.2. Extrusion and injection molding procedures for reference formulations

A CLEXTAL BC 21 twin-screw co-rotating extruder ($L = 1200$ mm, $L/D = 48$) was used for the introduction of additives into thermoplastic matrices. The extrusion was done at an adapted temperature of each formulation and with a rotation speed of 4.2 Hz using a 27 element screw profile with the rate of 5 kg h^{-1} . After exiting the extruder, the melted compounds were passed through a water bath and then chipped into pellet form. As in the extrusion step, the composites were dried for 12 h at 80°C under vacuum prior to injection molding in order that there was a polymer chain relaxation. After extrusion, 100×100 mm plates and pastilles of diameters 10, 20 and 30 mm respectively were injection molded using a SANDRETTO AT injection molding device. All the materials were 4 mm thick.

2.3. Instrument

The LIBS system was a commercial MobiLIBS (IVEA, France)[19]. The Nd:YAG laser (Quantel Brio) was employed at 266 nm and 532 nm delivering a maximum of 6 mJ and 33 mJ/pulse respectively. Pulse duration was 3 ns and a fixed frequency of 20 Hz. Spot diameters were measured at $50 \mu\text{m}$ for the 266 nm and $120 \mu\text{m}$ for the 532 nm. As the focusing system and the pulse duration are fixed on this system, the only parameter likely to change the irradiance was the energy selected by the operator. The light emitted by the resulting plasma was collected by a lens and an optical fiber and sent to an Andor echelle spectrometer (Mechelle 5000). This spectrometer has a resolving power of $\lambda / \Delta\lambda = 5000$. The diffracted light was then collected by an intensified charge coupled device (ICCD) camera (Andor iStar). The spectral range of this system was 200–975 nm. The Analibs™ software controlled the detection and laser firing. Argon (5.0 grade) and Helium (6.0 grade) were purchased from Linde gas.

The spectra were accumulated from 60 laser shots, a moderate number of laser shots was preferred in order to reduce the potential degradation of the polymer due to heat diffusion over the surface during measurement. All parameters: number of pulses, fluence, delay time, and integration time gate were optimized using classical univariate approach.

Table 1
Formulations of reference samples.

Matrix reference: polymer containing	Additives and concentration range				
	Br (bromide flame retardant) (1): TBBA	Cl (chloride flame retardant)	Ca (calcite)	P (phosphorus flame retardant)	Br (bromide flame retardant) (2):TBBA (73.3% mol) + Sb ₂ O ₃ (26.7% mol)
	(%) m/m	(%) m/m	(%) m/m	(%) m/m	(%) m/m
ABS1 Terluran GP22: acrylonitrile, 1,3-butadiene and styrene (A)	1–20	1–20	1–20	1–12.5	1–11
ABS-PC Sabic C2800: acrylonitrile, 1,3-butadiene, styrene and polycarbonate (C)	1–20	1–20	1–20	1–12.5	1–11
PP Apryl 3400 MA1: polypropylene (P)	1–20	1–20	1–20	1–12.5	1–11
HiPS Escrimo KG2: polystyrene (H)	1–20	1–20	1–20	1–12.5	1–11

Download English Version:

<https://daneshyari.com/en/article/7674920>

Download Persian Version:

<https://daneshyari.com/article/7674920>

[Daneshyari.com](https://daneshyari.com)