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Use of laser-induced breakdown spectroscopy for the determination of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) concentrations in PC/ABS plastics from e-waste

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ABSTRACT

Due to the continual increase in waste generated from electronic devices, the management of plastics, which represents between 10 and 30% by weight of waste electrical and electronic equipment (WEEE or e-waste), becomes indispensable in terms of environmental and economic impacts. Considering the importance of acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and their blends in the electronics and other industries, this study presents a new application of laser-induced breakdown spectroscopy (LIBS) for the fast and direct determination of PC and ABS concentrations in blends of these plastics obtained from samples of e-waste. From the LIBS spectra acquired for the PC/ABS blend, multivariate calibration models were built using partial least squares (PLS) regression. In general, it was possible to infer that the relative errors between the theoretical or reference and predicted values for the spiked samples were lower than 10%.

1. Introduction

The worldwide demand for technical plastics and the consequent accumulation of these residues from end-of-life products are constantly increasing. In 2013, the global production of plastic was approximately 300 million tons, showing an increase of 4% from 2012 (Anuar Sharuddin et al., 2016). The same behavior is exhibited by waste from electrical and electronic equipment (WEEE or e-waste) (Vazquez and Barbosa, 2016), which is growing exponentially and contains large amounts of plastic materials (Aquino et al., 2016).

The technical plastic fraction of WEEE is composed by more than 15 different polymers. However, acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and their blends are among the most important plastics used by the electronics industry (Buekens and Yang, 2014; Tarantili et al., 2010; Taurino et al., 2010), due to its good characteristics, which can be improved through the mixture of them. In PC/ABS blends, desirable features, such as the toughness and heat distortion temperature, are enhanced from PC, while ABS leads to better processability and cost reduction. For these reasons, PC/ABS blends are widely used in important industries, such as the electronics and automotive (Buekens and Yang, 2014; Kuram et al., 2016).

Regarding the management of plastic residue, which often contains hazardous flame retardants (Aquino et al., 2016; Shao et al., 2016), the option to dispose these materials in landfills has become increasingly undesirable, due to the low sustainability, high cost, and decreasing available space (Ignatyev et al., 2014; Vazquez and Barbosa, 2016). In this context, the recycling of PC, ABS, and their blends has been a target of research and practical action in the last years (Balart et al., 2005; Barthes et al., 2012; Farzadfar et al., 2014; Hopewell et al., 2009; Jing-ying et al., 2012; Kuram et al., 2016; Liu and Bertilsson, 1999; Tarantili et al., 2010).

Concerning the analytical aspects, it is evident that precise knowledge of the amount of PC and ABS in their blends is very important, from the early steps of recycling (identification/classification) to the analysis of the obtained product. In addition, precise, simple, and fast analytical methods are required in quality control laboratories in industry and research or academic centers.

Several strategies have been employed to determine the composition of polymer blends of PC/ABS. The presence of both polymers in the blends can be confirmed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), as

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two glass transition temperatures (*Tg*) are readily observed at 85–105 °C (ABS) and 150–155 °C (PC) (Adams et al., 1993; Babbar and Mathur, 1994). Mechanical analyses, such as impact and tensile tests, are also widely used (Krache and Debah, 2011; Kuczynski et al., 1994). However, these techniques are time consuming, require unusual sample preparation for an analytical chemistry laboratory, conditioning protocols prior to measurement, and present low analytical frequency. Near-infrared (NIR) has also been used to evaluate the proportion of PC and ABS in blends (Scaffaro et al., 2012); however, it is not suitable for the analysis of black plastic samples (Beigbeder et al., 2013; Maris et al., 2012; Masoumi et al., 2012; Roh and Oh, 2016). In this regard, laser-induced breakdown spectroscopy (LIBS) is an analytical technique that presents great potential for this application, due to the following advantages: high analytical frequency, portability, no or minimal sample preparation, and the possibility of hyphenation (Galbács, 2015; El Haddad et al., 2014).

LIBS is a multi-elemental technique in which a laser beam excites and intensively heats a small volume of the sample. The heated sample is converted to a gaseous plasma state and broken down into atoms, which produces a characteristic radiation of light. This light is analyzed spectrally, and through calibration, the intensity of the spectra indicates the concentration of the elements in the sample (Musazzi and Perini, 2014). However, some challenges are still present, such as the low availability of matrix-matched standards for quantitative analyses and pulse-to-pulse signal fluctuations that can lead to relative standard deviation (RSD) values higher than 10% (Aquino et al., 2016; Aquino and Pereira-Filho, 2015; Galbács, 2015).

Despite this, since 1998, a relative high number of publications have been presented methods for plastic identification using LIBS, particularly combining the use of different chemometric tools. Banaee and Tavassoli (2012), for instance, used a chemometric method based on discriminant function analysis (DFA) to identify polymers with slight differences among their spectra. Sattmann et al. (1998) used Artificial neural networks (ANNs) combined with LIBS with success to identify polymers. Lasheras et al. (2010) used with success the methods of normalized coordinates (MNC) and linear and rank correlation to identify polymers with very similar chemical compositions. Other chemometric tools such as soft independent modeling of class analogy (SIMCA), k-nearest neighbor (KNN) and partial least squares for discriminant analysis (PLS-DA) have been widely used in the identification and classification of polymers (Aquino et al., 2016; Aquino and Pereira-Filho, 2015; Costa et al., 2017). Determining the ratios of different emission lines and molecular bands associated with the use of principal component analysis (PCA), was a strategy found in the literature for identification and classification of polymers (Grégoirie et al., 2011; Unnikrishnan et al., 2013; Xia and Bakker, 2014).

However, these above mentioned chemometric tools are limited to classification models proposition for the identification of samples according to their similarity. Thus, its application for quantitative analysis of PC and ABS in blends associated to chemometric tools is not reported in the literature. In this sense, partial least-squares (PLS) technique is often used for the analysis in multivariate calibration methods aiming quantitative analysis of various analytes (Mota et al., 2015; Viegas et al., 2016). PLS multivariate calibration is strongly used in combination with near-infrared (NIR) spectroscopy. Sulub and DeRudder (2013), for example, determining the concentration of polycarbonate and rubber in blends of these materials using PLS models NIR. Thus, the present study shows and discuss a new application of laser-induced breakdown spectroscopy (LIBS) using PLS for fast and direct determination of the amount of PC and ABS in blends of these materials obtained from samples of e-waste.

2. Materials and methods

2.1. Laser-induced breakdown spectroscopy (LIBS)

LIBS spectra were obtained using a J200 LIBS system (Applied Spectra, Fremont, CA, USA) controlled by the Axiom 2.5 software (Applied Spectra). This instrument consists of a 1064 nm Nd:YAG laser and a 6-channel charge-coupled device (CCD) spectrometer recording spectra information from 186 to 1042 nm. Channel 1 goes from 186 to 309 nm, channel 2 from 309 to 460 nm, channel 3 from 460 to 588 nm, channel 4 from 588 to 692 nm, channel 5 from 692 to 884 nm and channel 6 from 884 to 1042 nm. The spectral resolution is <0.1 nm from UV to VIS and <0.12 nm from VIS to NIR. The Axiom 2.5 software from the same manufacturer controlled the operational parameters of the equipment. These parameters were the laser pulse energy, which ranging from 0 to 100 mJ, the gate delay - the time interval between the incidence of the laser pulse and the start of signal recording by the spectrometer – ranging from 0 to 2 μs, and the spot size, ranging from 50 to 250 μm. The Axiom 2.5 software also manages the movement of the sample, assisted by an automated XYZ stage and a 1280 × 1024 complementary metal-oxide semiconductor (CMOS) color camera imaging system. The software at 1.05 ms establishes the gate width, which is the time interval that the spectrometer registers the emission signals.

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed on a Netzsch F3 200 Maia DSC (Netzsch-Gerätebau GmbH, Selb, Germany) instrument under nitrogen purge. Scanning analysis was carried out from 20 °C to 200 °C with heating and cooling rates of 20 °C·min^{-1}. The glass transition temperature (T_g) was determined during the second heating by the inflection method.

2.3. Blend and sample preparation

The multivariate calibration model was built using a set of 11 mixtures of PC/ABS in the following proportions: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100 (w/w%). These mixtures were prepared according to the following procedure:

i) Individual dissolution of PC (polycarbonate Lexan 101, Sabic Company, Campinas, Brazil), ABS granule resin (Cycolac EX 58 Sabic Company, Campinas, Brazil), and sample pieces in dichloromethane (p.a. ACS reagent, Sigma-Aldrich, St. Louis, MO, USA) until obtaining a 10% w/v solution.
ii) Attainment of polymer/sample chips after dichloromethane evaporation, and spreading the solution on a glass plate under air flux at room temperature (25 °C).
iii) Attainment of polymer/sample powder through grinding the chips in an analytical mill at 28,000 rpm, and subsequent sifting of the gross powder through a stainless-steel mesh sieve (0.5 mm).
iv) All mixtures or sample pellets were prepared using 0.5 g of the respective powder material. This mass was added in an aluminum mold and heated in a thermopress at 200 °C for 10 min with a pressure of 0.4 metric tons. Additional details of this procedure are available in a previous publication (Aquino et al., 2016).

To evaluate the multivariate calibration model, 6 plastic samples containing only ABS (black and white pieces) obtained from scraps of a telephone, keyboards computer, two computer casings

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