



Classification of plastic materials by imaging laser-induced ablation plumes[☆]



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ABSTRACT

A method of rapid classification and identification of plastic materials has been studied in this work. Such method is based on fast spectroscopic imagery of laser-induced ablation plume on plastics to be analyzed. More specifically, a classification schema has been developed first according to the nature of the CC bonds which characterize the polymer matrix. Our results show that the spatial distribution and the evolution of the molecular species in the ablation plume, such as C₂ and CN, exhibit clear different behaviors for polymers without any native CC bond, with CC single bonds or with CC double bonds respectively. Therefore the morphological parameters of the populations of the molecular species extracted from the time-resolved spectroscopic images of the plumes provide efficient indicators to classify the polymers characterized by the above mentioned different kinds of CC bonds. When dealing with different polymers with the same kind of CC bond, CC single bond for instance, other indicators should be introduced to provide the further discrimination. Such indicators can be for example a specific native molecular bond other than CC bonds, CN for example, the total emission intensity of which may exhibit specific time evolution. The robustness of the developed classification schema has been then studied with respect to two of the most frequently used additives in plastics fabrication, graphite and titanium. Our results show a negligible influence of these additives in the morphology of the populations of the molecular species when such additives are mixed into the polymer matrix with the percentages usually used in plastics productions, which demonstrates the validity of the developed classification schema for plastics.

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1. Introduction

Recycling of plastics offers an efficient solution to reduce plastic pollutions in the environment as well as the consumption of the natural resources, which represents an important issue for the sustainable development. It poses nevertheless technical challenges especially for sorting such materials before their recycling because of the similar physical properties of plastics. Classical methods of separation of solid state materials by differentiation in density or magnetic attraction, suitable for metallic materials, totally lose the efficiency. Indeed plastics are basically characterized by their polymer matrix, which, in the point of view of elemental composition, always consists of a limited number of nonmetal elements such as H, C, N, and O. Only the molecular structure of the macromolecules constituent of a polymer, i.e. the way in which the above mentioned elements are linked between them to form a macromolecule (monomer), is characteristic of a type of polymer. In addition fillers or additives, such as graphite and titanium, can be mixed

into polymer matrix according to the specific properties targeted of a given plastics. The lack of mature automatic sorting technology today leads to the current need of manual sorting of plastic materials, which is, beside of the inefficiency, often implemented with harmful working conditions for the operators. Sorting machines which allow either assistances to manual sorting with a safer working environment and a higher efficiency or, more ideally, fully automatic separation of plastics, are currently searched and represent a future solution for this crucial societal need.

Different processes have been investigated to provide the principles for efficient automatic sorting machines of plastics. Classification with the electrostatic property of polymeric materials has been described [1]. Optical methods are generally considered as the basis of more stable and efficient separation technologies [2]. More specifically, near-infrared (NIR) spectroscopy determines the molecular structure of a polymer by detecting the reflected or transmitted radiation [3–6]. However, this technique is quite sensitive to the color (dependent to the additives) of the plastics as well as their surface contamination [7]. More recent developments explored the auto fluorescent property of some polymers or fluorescence emission from doping fluorophores [2,8,9]. The lifetime of the excited fluorescence is thus used as the indicator of the polymeric material [10,11]. Nevertheless the method cannot be applied to any

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plastics without labeling fluorophore. Elemental analysis technique such as X-ray fluorescence spectrometry (XRF) has been used to detect certain polymers such as polyvinyl chloride (PVC), which is characterized by the presence of specific nonmetals such as chlorine [12].

Laser-induced breakdown spectroscopy (LIBS) has been considered as the basis of plastic material sorting technology. In fact LIBS shares the characteristics of all the above mentioned optical methods to be able to provide direct and rapid analysis of plastics. Moreover, it is capable to simultaneously provide elemental as well as molecular spectroscopic information, which is especially interesting for the analysis of organic materials such as plastics. Indeed, as an eminent elemental analysis technique, LIBS has been also demonstrated to be suitable to reveal molecular structure of organic materials [13–15]. The combination of elemental and molecular emissions, especially those of C_2 and CN radicals, offers an ensemble of spectral features to characterize plastics and organic materials in general [16–22]. More recently a variant of LIBS technique has been introduced and validated to correlate the molecular structure of a polymer to the distribution and evolution of the populations of molecular species, C_2 and CN, in the ablation plume [23]. Such distributions can be directly recorded with an intensified CCD (ICCD) camera associated with narrowband filters, resulting in spectroscopic images of the molecular species [24]. The demonstrated principle greatly simplifies the experimental arrangement by removing the spectrometer necessary in a LIBS setup, which represents an advantage for real applications.

In this work we develop a schema of classification and identification of plastic materials based on the above mentioned principle of relating the molecular structure of a polymer to the spectroscopic images of the molecular species observed in the induced ablation plume. Such schema first distinguishes polymers according to the nature of the characteristic CC bonds of the polymers. A further separation is then performed among polymers with the same characteristic CC bonds. The method is first demonstrated with pure polymers. Its robustness is then studied with the corresponding plastics containing additives, graphite and titanium, at percentages usually used for plastics production. In the experimental point of view, an improved dual-wavelength differential spectroscopic image system was specially built for the experiment, which allowed the pair of on- and off-images for a given species in an ablation plume to be taken simultaneously.

2. Experimental

2.1. Preparation of the samples and their characteristics

The samples used in this experiment were prepared by CRITT-Matériaux-Alsace. Raw material powders were injected into a press with two heating platens which transformed the loaded power materials into a plate of corresponding polymer or plastics with a thickness of 0.5 cm to 1 cm. Two sets of samples were thus prepared. A first one consisted in four pure polymers representing four families of polymers with different types of CC bonds as shown in Fig. 1: (a) Polyoxymethylene (POM) without any CC bond, (b) Polyethylene (PE) and (c) Polyamide (PA) with single CC bonds, and (d) Polystyrene (PS) with single and double CC bonds. A second set of samples included plastics prepared by adding titanium dioxide or graphite in pure PE to obtain different elemental concentrations of Ti and C in the range of 0.001 to 5 weight percentage. These two additives are widely used for functionalizing plastics. Polymer granules and additive powders were mixed in a blender (Haacke Polydrive technology) in order to make a homogeneous paste before pressing it into a plastic plate.

2.2. Experimental setup

A detailed description of the experimental setup can be found elsewhere [25]. Briefly, we used a Nd:YAG laser (QSmart, Quantel Technology) at the fourth harmonic (226 nm) for ablation with a pulse energy of 5 mJ, pulse duration of 5 ns and a repetition rate of 5 Hz, which took place in the ambient atmosphere (required by the targeted applications). The small ablation laser energy used was to enhance the production of molecular fragments in the ablation plume. The pulse energy was kept constant with an active optoelectronic servo system, insuring a low standard deviation of the pulse energy of 0.15 mJ. Laser pulses were focused by a fused silica lens of 75 mm focal length. The laser beam was focused into the sample with a shift of 600 μm with respect to its surface, resulting in a beam diameter of about 130 μm on the sample surface, to avoid direct breakdown in the atmosphere and obtain a stable plasma. Such focusing resulted in a fluence of about 38 J/cm², corresponding to an irradiance of 7.5 GW/cm². The distance between the focusing lens and the sample surface was kept constant

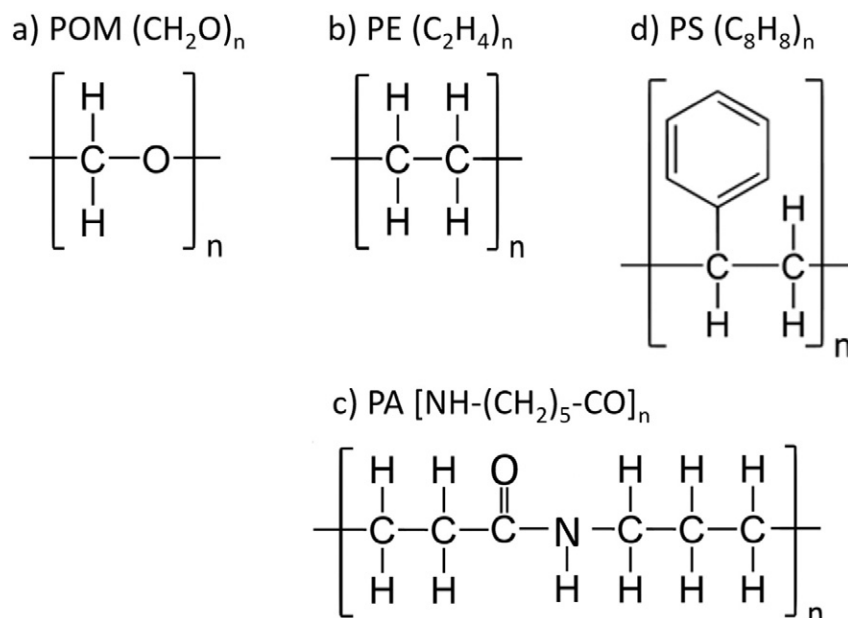


Fig. 1. Structure diagrams and chemical formula of the studied polymers. (a) Polyoxymethylene (POM), (b) Polyethylene (PE), (c) Polyamide (PA) and (d) Polystyrene (PS).

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