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A quantitative differentiation method for plastic bags by infrared spectroscopy, thickness measurement and differential scanning calorimetry for tracing the source of illegal drugs

Valerio Causin [a,*], Carla Marega [a], Pietro Carresi [b], Sergio Schiavone [b], Antonio Marigo [a]

[a] *Dipartimento di Scienze Chimiche dell'Università, via Marzolo 1, 35131 Padova, Italy*
[b] *Sezione di Chimica, Esplosivi ed Infiammabili, Reparto Carabinieri Investigazioni Scientifiche, Viale Tor di Quinto, 151-00191 Roma, Italy*

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Abstract

Fifty shopping bags, commonly encountered in the packaging of drug doses, were characterized by thickness measurements, infrared spectroscopy and differential scanning calorimetry. By these very straightforward and inexpensive techniques, without sample preparation, nearly all the considered samples could be discriminated. Ninety-seven percent of the possible pairs of white, apparently similar dull polymer films were differentiated. The rather large degree of variability existing in grocery bags, even though they are mass produced, was shown, confirming that these items can be useful in tracing the source of illicit drug doses.

Keywords: Forensic science; Plastic materials; Drug packaging; Polymers; Polyethylene; Infrared spectroscopy; Differential scanning calorimetry

1. Introduction

The characterization of plastic packaging material may be a problem of relevant importance in forensic science. Plastic bags are used to conceal body parts of a victim or other crime related materials [1] and to pack illicit drugs [2–4] and may be of interest in arson related investigations [5,6]. In particular, a thorough examination of the packaging used to contain drugs can help in tracing their source. In order to be useful, though, the characterization of such materials should be complete enough to discriminate apparently similar plastic films, differing by manufacturer or manufacturing batch. An assessment of which characteristics are less common, and thus more significant, is important to determine the evidential value of the forensic results presented to the Court. The more of these features the items are found to have in common, the greater are the chances that they came from the same single source.

Polymers are quite versatile materials under this point of view, because slight variations in the production process may bring about a variety of differences in chemical and physical properties that may be exploited for forensic science purposes [6–12].

A number of methods have been proposed for the analysis of plastic packaging films, among which UV–vis [2] and infrared (IR) spectroscopy [2], differential scanning calorimetry (DSC) [5], pyrolysis–gas chromatography [13], gas chromatography–mass spectrometry [14] and elemental analysis [15,16], but their effectiveness in discriminating specimens of the same polymer basis (i.e. mass produced articles) has rarely been accounted for.

The purpose of this paper is to show that a combination of widely available and inexpensive techniques such as IR spectroscopy, DSC and thickness measurement can discriminate apparently similar grocery bags. These bags are quite often used by Italian drug smugglers for packaging of individual doses. A number of times our labs were requested by the Court to correlate cut plastic bags seized in the smuggler's premises with the portions of plastic film that wrapped the illicit substances that had been sold to the drug-addicts of the zone.

* Corresponding author. Tel.: +39 049 8275153; fax: +39 049 8275161.
E-mail address: valerio.causin@unipd.it (V. Causin).

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Fifty shopping bags of different shops were analyzed, produced by different manufacturers. Inter- and intra sample variations were investigated, along with the diversity among samples of the same lot or from different batches of the same producers.

2. Experimental

2.1. Samples

All the major supermarket chains in the Venice, Italy, region were visited to obtain samples of shopping bags. A number of plastic bags were also acquired in medium and small-size shops. A total of 50 samples were collected from 31 different stores, 16 of which were colored. The manufacturer and batch code, when present on the plastic film, were noted and recorded.

2.2. General examination and thickness measurements

The films were visually observed by the naked eye and under a DM4000M (Leica) microscope under cross polarized light in the transmission and reflection mode. The thickness was measured by a Digico 1 (Tesa) micrometer, with a $\pm 2\,\mu m$ precision. A single layer of plastic was measured for each sample. Five replicates were acquired and the average was calculated. The standard deviations computed on the basis of replicate data were always smaller than the precision of the instrument, so an error of $\pm 2\,\mu m$ was associated to the averages.

2.3. Infrared spectroscopy

IR absorption spectra were acquired on a Nexus FTIR spectrometer (Thermo Nicolet) in attenuated total reflection (ATR) mode with a smart endurance accessory (Thermo Nicolet) equipped with a diamond ATR crystal. A MIR Globar source was used and the detector was of the DTGS type. The spectral region spanned from 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1}. Two hundred and fifty-six scans were collected in the acquisition of the IR spectrum of each sample. Nicolet Omnic software was used for the treatment of spectra. The ATR correction routine of the Nicolet Omnic software was applied to ATR data.

2.4. Differential scanning calorimetry

All the measurements were carried out with a model 2920 calorimeter (TA Instruments) operating under N_2 atmosphere. Tiny portions of the samples, weighing about 5 mg, were closed in aluminum pans. A heating rate of 10 °C/min up to 200 °C was set in order to observe the polymer melting peak. After erasure of thermal history by a 5 min isotherm at 200 °C, the sample was cooled down to room temperature at 10 °C/min and heated again to 200 °C at the same rate. Indium of high purity was used for calibrating the DSC temperature and enthalpy scales. The choice of the baseline in enthalpy evaluations has been standardized for all samples. In order to quantify the repeatability of the measurements, five replicates were recorded for selected samples (Aa1, B, D, F and M) and their standard deviations were computed. A 3% error on the enthalpy associated to melting endotherms and a 2% error on the enthalpy of crystallization was obtained. All the remaining samples were analyzed twice, a third confirmation replicate was performed if the two previous measurements differed by more than 3% in case of melting peaks or 2% in case of crystallization exotherms.

3. Results and discussion

A visual examination of the samples collected was the first step of the characterization procedure adopted in this work. Of the 50 samples collected, 16 were colored in shades that were readily distinguishable by the naked eye. The appearance of the film (shiny or dull) was noted, along with features like cuts, folds, perforations or seals. Only one textured bag (sample O) was encountered in the survey of the shops visited during the sampling campaign, making this feature a quite significant one when evaluating comparisons. The existence of machine marks and defects in the printing of some bags was observed and recorded, and could be of interest in casework in which comparisons were requested between whole bags used for the packaging of drugs [2]. Moreover, the name of the manufacturer and the lot number was often printed on the bag, a detail that could be of great help in cases like those mentioned before. The work reported in this paper was aimed at a different type of comparison, in which it must be determined if different film portions were cut from the same bag. This is the analysis most widely requested by Italian Courts, because they are often interested in linking a dealer, who prepared and packed single doses from a quantity of drugs, to the drug-addicts to whom the doses were sold. Pieces of plastic film are also known to be used for the drug packages ingested by ''body stuffers'' [3,4], so their characterization can be exploited in reconstructing the dynamics also of international traffic of illegal substances. To the knowledge of the authors, no systematic study was reported on the European market about this specific type of forensic analytical problem.

After a simple visual examination step, 34 white and dull samples appeared indistinguishable and thus requested a more thorough instrumental characterization. Table 1 shows the characterization data collected for these samples. Each specimen was identified by a capital letter that designates the shop that supplied it. A lower case letter was added to the code of the sample if different manufacturers produced bags for the same shop. Samples Aa1 and Aa2 were supplied to the same shop by the same manufacturer but differed in size. The data shown in Table 1 are the average of the various replicates performed on each sample. When more than one specimen was available, as in the case of products coming from different lots (vide infra Table 2), the datum shown is the average of all the measurements that were carried out.

By IR spectrometry it was found that all the considered bags were made of polyethylene (PE). Although the polymer matrix was the same for every sample, an examination of IR spectra showed that additives were sometimes present, so that three