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Polymer tracer detection systems with UV fluorescence spectrometry to improve product recyclability

E. Maris [a,*], A. Aoussat [b], E. Naffrechoux [c], D. Froelich [a]

[a] Laboratoire Conception Produit Innovation, Chambéry (LCPI), Institut ARTS et METIERS ParisTech Chambéry, Savoie Technolac, 4 Rue du Lac Majeur, F-73 375 Le Bourget du Lac Cedex, France
[b] LCPI, ARTS et METIERS ParisTech Paris, France
[c] Laboratoire Chimie Moléculaire Environnement (LCME), Université de Savoie, F-73 376 Le Bourget du Lac, France

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ABSTRACT

The recycling of materials originating from end-of life products is essential to preserve our raw material resources, which are increasingly expensive and whose extraction is increasingly impactful for the environment. However, certain materials are still not recycled today. In the case of plastics, their recycling includes grinding, which generates complex mixtures. It is not possible to sort these mixtures and reach a high degree of purity with the existing physico-chemical processes. Automated sorting processes using near infrared spectroscopy are limited to dark-colored materials. One option is to add tracers to virgin materials to allow identification and rapid sorting of end-of-life products, using UV fluorescence spectrometry as the identification technique. The optimization of the polymer/tracer/detection system is based on several criteria: the reliability and speed of detection of UV fluorescence tracers added to a polymer matrix with carbon black, the relevance of the environmental impact of the tracers, and the preservation of the mechanical properties of the polymer with the tracers added.

1. Introduction

Certain oil and mineral resources are becoming increasingly rare and expensive to extract, and their extraction has increasingly serious environmental impacts on both the ecosystem and human health. As many studies have shown, improving a product's recyclability is one of the ways to limit environmental impacts and material costs. The production of recycled materials makes it possible to save over 80% in energy in comparison with that required for virgin materials (Fig. 1), and to avoid considerable greenhouse gas emissions.

Despite the development of product eco-design (Millet, 2003; Tonnelier et al., 2007) and the improvement of recycling technologies, polymers are recycled very little today. Why? Firstly, crushing processes produce complex mixtures. It is not possible to sort these complex mixtures and achieve high purity rates with the existing physico-chemical methods (Reuter et al., 2006), and spectrometric methods do not allow the sorting of dark-colored polymer materials. In 2009, 24.3 Mtons of plastic waste were generated in Europe, and only 22.5% on average were recycled in all sectors combined (PlasticsEurope, 2010).

The presence of impurities in the polymers due to poor sorting quality impacts the performance of the recycled material. Good recycled material quality is required in order to find "noble" outlets and expand the number of opportunities to use a high-performance, safe material with an economic value close to that of virgin plastics.

Finally, in today's context, many mass consumption products escape collection or are treated in medium-sized facilities. Mass quantities of recycled plastics are not available. It is therefore necessary to find compromises between the sorting level (by matrix, by additive, etc.), the properties and the volumes generated in order to meet the demands of the key players in the market.

To overcome these technological limitations, one possibility is to add specific tracers to polymer families to facilitate their rapid, automated industrial sorting using UV fluorescence spectrometric sorting. The research problematic is to determine the criteria for selecting the polymer candidates for recycling and detection conditions in line with the choice of tracers.

In 2008, a first study entitled TRITRACE focusing on the detection of tracers in colorless and black polypropylene and white ABS was carried out with the industrial partners SEB Group, Plastic Omnium, and Tracing Technologies, and two laboratories, the ITECH and the *ARTS et METIERS ParisTech* Institute in Chambéry. Two patents (Lambert and Hachin, 2010a,b) were registered. The study was continued in 2010 though a program financed by the French National Research Agency (ANR) and expanded to include other tracers and polymer families.

The initial results of these two projects are discussed in this paper. A description of the polymer tracing process for recycling

* Corresponding author.
E-mail address: elisabeth.maris@ensam.eu (E. Maris).

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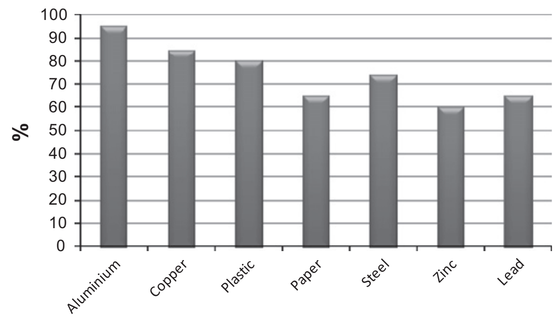

Fig. 1. The use of recycled material saves energy compared to the use of virgin material (BIR, 2009).

is presented with a state of the art of the tracing techniques used for recycling. The concept of tracing for the purposes of material recycling was defined and experimented. The approach of this study consisted of different steps: firstly to define the appropriate polymer candidates, secondly to determine the tracers according to the number of polymers chosen and according to technical criteria such as the intensity of the light sources available enabling tracer excitation and the sensitivity and speed of the detection systems receiving the fluorescence signals. Two polymers containing two tracers and two white and black colorants were tested. Tests results were conducted to validate fluorescence detection and the mechanical preservation of properties before and after aging of the samples in accordance with the specifications of the automotive and household appliance sectors.

List of polymers
ABS: Acrylonitrile–butadiene/styrene
PA: Polyamide
PC + ABS: Polycarbonate + ABS blend
SAN: Styrene acrylonitrile
PA 66: Polyamide 66
PP copo, P/E: Polypropylene copolymer
HIPS: High impact polystyrene
LDPE: Low density polyethylene
HDPE: High density polyethylene

2. Description of the polymer tracing process for recycling

2.1. Bibliographical research

Several studies have been published on tracing technologies for polymers recycling. The development of the concept of a virgin polymer tracing system for sorting began in 1993. The first patent registered (British Petroleum Company, 1993) describes a method to identify polymers by detecting the fluorescence of certain tracers composed of rare earths in the near-infrared spectral range (NIR) between 700 and 900 nm for tracer concentrations from 0.001 ppm to 1 ppm. The source used is a laser diode emitting in the NIR at 670 nm. The disadvantage of this method is its difficulty to detect a signal in the NIR when the matrix has a dark color. The carbon black used as a colorant absorbs all of the rays in the NIR (Eisenreich et al., 1992).

A patent registered in 1994 (Bayer, 1994) describes two tracer systems with different fluorescence emission wavelengths, with tracers with different fluorescence durations for each system. The identification principle allows codification with four tracers. This method is currently used in the biochemical sector. The experimental system includes a flash lamp and a programmable camera to defer the shooting of the image by a few nano-seconds after excitation by the source. This system thus enables the identification of molecules that have the same fluorescence emission wavelength but not the same duration. This method appears difficult to install in a rapid, automated sorting system, since with industrial systems there is continuous light on the samples to be sorted, making it impossible to differentiate the fluorescence durations in order to differentiate the tracers.

In 1998, another study (Simmons et al., 1998) (Ahmad, 2004) financed by a European program led to a first pilot system to sort plastic bottles in the packaging sector. With this system, thanks to a codification based on combinations of three tracers with concentrations raging between 0.5 and 20 ppm, it was possible to identify bottles made with PEHD. Patents for this identification system were registered by the program partners (Lambert and Hachin, 2004). The pilot bench did not enable the identification of dark-colored tracers, and no test was carried out on other types of polymer matrixes.

In 2007, a study was carried out on the state of the art of the different tracing technologies (Froelich et al., 2007a,b). Two technologies were validated to sort black polypropylene: magnetic tracer detection and X ray fluorescence detection of tracers made from rare earths. In 2008, a thesis was financed by the French Environment and Energy Management Agency (ADEME) to conduct laboratory tests on X fluorescence detection (Bezati et al., 2010). The results of this research showed that detection with magnetic tracers is industrially viable but does not allow codification with several tracers. X fluorescence detection enables the detection of tracers based on rare earth oxides at concentrations of 1000 ppm in black or painted polymers. The absorption of the X fluorescence by the molecules of the ambient air makes it impossible to decrease the concentrations of tracers to below 100 ppm, and detection times are still long with respect to the industrial constraints of rapid sorting. The choice of tracers is limited to rare earths.

In conclusion, all of these different studies validated the polymer tracing technique. Certain aspects of the fluorescence of polymer tracer systems must be explored in further depth, such as possible signal attenuation phenomena due to the interaction between tracers, polymers and their additives such as carbon black, the influence of polymer aging on fluorescence, and the choice of tracers with a lesser impact on natural resources.

2.2. The concept of material tracing for recycling

This technique makes it possible to identify a material thanks to the signature of a tracer and not its intrinsic properties, and is already used to authenticate objects such as banknotes.

Polymer tracing consists of incorporating into a material a small concentration of a substance with specific luminescence properties after irradiation by a light source, and carrying out a spectrometric analysis of the signal of the substances incorporated in the material in order to identify them according to the positive or negative signal (Fig. 2).

The concept of polymer tracing for recycling is different from that of the marking of polymer parts in accordance with ISO 11469 2000: “Generic identification and marking of products made of plastic materials”. Following this standard, new parts are engraved with a code enabling the identification of their materials, in order to recycle parts after manual sorting.

The polymers that are candidates for tracing are those recognized as difficult to sort with the current physico-chemical sorting or optical sorting technologies. They are essentially polymers that are dark-colored and have similar densities, or that have fillers that