Marker materials and spectroscopic methods for sorting plastic waste

Introduction

The application of plastics as industrial and consumer goods is very diverse as plastics have excellent mechanical, thermal, and chemical properties and can be produced cost-effectively in large quantities. Since 2005, global production of plastics has increased from 230 to 367 million tonnes in 2020.1, 2 Plastics are currently used primarily in the packaging sector (40.5%), the building and construction sector (20.4%), the automotive sector (8.8%), and in electrical and electronic equipment (6.4%).3 The remaining 24.1% can be found in other sectors, with each using less than 5% of the total amount of plastics.4 The recycling rate of plastic packaging in the EU (EU 27) is 39.7% (based on data from 2020).5 This means there is still some catching up to do to meet a 55% recycling rate for plastic packaging (70% for all packaging) in 2030.6 It is estimated that approximately 60% of all plastics produced globally between 1950 and 2015 was improperly disposed of or landfilled.4, 5, 6 Furthermore, careless littering of used plastics leads to fragmentation of the plastics through mechanical and chemical environmental influences, such as UV radiation, and thus to the formation of microplastics or nanoplastics.7 These microparts can in turn release various additives (plasticisers, flame retardants, dyes and others), which can endanger human health and sensitive ecosystems.7

As a countermeasure, the EU’s Circular Economy Action Plan (CEAP) provides for the monitoring and treatment of plastic waste as well as product labelling and an increase in recycling rates — in addition to banning primary microplastics in products (such as exfoliating granules).8

For the material recycling of plastics, it is generally very important that used plastics are separated by type and recycled. This dossier provides an overview of advanced materials with spectroscopic “fingerprints” and suitable detection methods that can be used for marker-based sorting.

Tracer-based sorting (TBS)

TBS is a technical solution to identify and separate types of plastic that could not be recognised by existing sorting systems until now. TBS refers to a methodology of material sorting in which so-called marker materials are already incorporated into or onto the plastic to be sorted during its production. These marker materials give the material special properties and only serve the purpose of targeted detection by spectroscopic methods (see Table 1). TBS can therefore be used directly for the targeted, automated, sensor-based sorting of a specific type of plastic from waste streams.9, 10 For over 30 years, organic fluorescent dyes have been used as tracers or marker materials. For example, since 1992 S.R. Ahmad and his research team have been working on solutions to optimise the automated detection and sorting of post-consumer plastic waste, where detection is mainly facilitated on
the basis of identifying fluorescence signatures of intrinsic chromophores or added fluorophores. Since then, numerous research projects, such as “BRITE-EURAM” or “MaReK” (marker-based sorting and recycling system for plastic packaging), have looked at the application of TBS in great depth.

Tracer or marker materials

The most important component of TBS is the so-called marker. These organic or inorganic substances facilitate the detection in the carrier matrix or in specific polymers. Rare earth elements are one promising class of substances that can be detected using X-ray fluorescence and near-infrared spectroscopy, photon upconversion (UC), and laser-induced breakdown spectroscopy (LIBS). Elements of this group are increasingly used in high-tech products because of their fluorescence and semiconducting properties.

In addition to the fundamental property of being detectable by already established detection methods, other parameters must be considered when selecting markers. The most important parameters include availability, material costs, service life, environmental sustainability and impact on the environment, and various physicochemical parameters (e.g. thermal stability, density, fluorescence yield, etc.). The possibility of recovery or recyclability of the marker from the plastic matrix should also be considered. An existing authorisation of a substance in accordance with European chemical legislation (REACH and CLP regulations) is also relevant for companies processing plastics, as it simplifies the use of the substance as a marker. Figure 1 shows a possible decision tree for the selection of potential markers, which was developed in more detail within the research project “PLASTMARK.”

Detection methods for TBS

Spectroscopic detection methods have long been used to identify and separate different materials. Mechanical recycling facilities for used plastics primarily use NIR sensors. However, sensors that detect in the ultraviolet (UV) and visible range (UV-Vis) or that are tuned to RAMAN spectroscopy, photon upconversion or X-ray fluorescence analysis can also be used. TBS requires a detection method or a combination of several sensor techniques capable of detecting the markers that are integrated into the plastic matrix. In this context, it is important for the recycling plant to achieve a sufficiently high throughput capacity or sorting speed. Table 1 summarises the spectroscopic methods that can be used to detect the marker or tracer materials. The applied technological assessment – not taking possible implementation costs into consideration – was carried out on the basis of the so-called technology readiness level (TRL). The TRL is measured on a scale of 1 to 9 and was developed by NASA in the 1970s as an indicator of the stage of development in space technology. By now, it has been adapted for many other sectors. Basically, the higher the TRL of a technology, the more advanced it is. In other words, a TRL of 8 is defined as a “system complete and qualified”. TRL 9 is then understood to mean suitability for mass production or industrial-scale application.

It should be noted that not all methods summarised in Table 1 have already been successfully tested or applied on an industrial scale in the sense of TBS. Consequently, there is still a great need for research. In general, the various methods can also be combined with each other to detect different contaminants or recyclable materials in the waste stream. At present, multispectral sensors for hyperspectral imaging and other detection methods, such as RAMAN or LIBS, are being researched extensively.

Figure 1: Proposed decision tree for the selection of marker materials that would be considered for specific plastic streams.
Economic aspects

For the large-scale implementation of TBS concepts, economic aspects regarding material costs for the marker material as well as very high investment costs for the conversion of the recycling facilities are crucial. Using a substance already registered as a marker in REACH has the advantage that the registration costs (including the necessary toxicity tests and documentation) are eliminated. For an annual import or production volume of 100-1,000 tonnes, these costs amount to around €800,000 and more on average. Another economically very important aspect is the high investment costs for the detection and sorting units that would be necessary for large-scale implementation in (existing) recycling plants, especially if the chosen methods have a low TRL. The TRL is also an indicator of the R&D costs for the improvement of a sorting technology up to the large-scale implementation of such TBS systems. In principle, it can be assumed that increases in TRL will also result in strong increases of the R&D costs. Nevertheless, TBS systems that already have a high TRL are advantageous from an economic point of view, as further development costs are saved. These additional costs resulting from the TBS implementation could possibly be offset in view of an “EU plastic tax” of currently €0.80 per tonne of nonrecycled plastic. However, more detailed cost analyses or profitability calculations would have to be carried out for this.

As with almost all new technologies, existing technical, environmental, and social barriers to TBS must also be overcome, and relevant stakeholders must be convinced to invest the necessary resources. For example, relevant stakeholders have already been asked about market drivers and barriers with regard to TBS as part of a study. In this survey, “regulatory and legal barriers”, “distribution of costs and benefits”, “profitability and competition”, “quality and safety aspects”, and “procedures and technical issues” emerged as the most critical concerns.
The above-mentioned study also presented two scenarios in more detail: “TBSlight” and “TBScomplete”. In the “TBSlight” scenario, TBS machines are introduced at the end of the already established sorting process to remove problematic materials such as composites. In the “TBScomplete” scenario, TBS machines completely replace conventional sorting technologies to enable single plastic streams with very high purity.

The study acknowledges that a future implementation of “TBSlight” (when compared with “TBScomplete”) is much more probable, as the already existing recycling system was considered too inflexible to actually realise the technically “radical” changes for “TBScomplete”. However, it was also mentioned that “TBSlight” is not sufficient to be able to achieve the legally binding recycling targets and the desired reduction of the carbon footprint.58,15

**Conclusion**

Tracer-based sorting (TBS) is a promising concept or technical measure that has the potential to meet the recycling targets of specific waste streams, such as technical plastics from waste electrical equipment, using innovative detection methods. For this, spectroscopy-based methods such as NIR, spectroscopy in the ultraviolet and visible range, photon upconversion or X-ray fluorescence can be used for fully automated sensor-based sorting of used plastics. The marker materials with so-called fingerprints* would be integrated directly into the polymer. The challenge here is to develop a standardised marking code – similar to the Resin Identification Code (RIC) – to enable uniform marking and sorting by several producers, suppliers, and sorters. According to our study46, rare earth elements such as cerium or yttrium oxide are suitable for marker application; in view of the EU chemicals legislation (REACH and CLP regulations), sound data is available on relevant physicochemical parameters and potential toxicity. Moreover, the organic dye perylene3,4,9,10-tetracarboxylic dianhydride could also be marketed as material and plastic products. As this marker has a specific fingerprint in the NIR spectrum. However, successful large-scale implementation of such TBS concepts would have to be investigated in more detail within the framework of feasibility studies. From an environmental, safety, and economic point of view, special consideration should be given to the carry-over or continuation/perpetuation of the marker materials during multiple recycling cycles. In summary, the aim should be to prove that TBS significantly improves the homogeneity of a waste plastics stream and thus increases the material quality and the yield of high-quality recycled materials. During this process, undesirable cross-contamination into other types of plastics must be avoided and the traceability of the markers guaranteed. Finally, if TBS technology is to be implemented successfully in the future, economic efficiency of TBS implementation must also be investigated.

* Unique combination of markers. By assigning marker fingerprints to individual plastic products with the same composition, the mixing of plastics with different compositions can be avoided and a high degree of purity can be achieved.

**Anmerkungen und Literaturhinweise**


