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Inorganic fluorescent marker materials for identification of post-consumer plastic packaging

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ABSTRACT

Current plastic packaging waste management practices in Europe, but also in other countries require improvement due to legal and societal requirements. To meet high recycling rates, significant changes among others in post-consumer packaging waste sorting become necessary. This waste stream is dominated by plastic packaging. Inorganic fluorescent tracer materials (oxide crystals doped with ytterbium Yb^{3+} sensitizer ions and either erbium (Er^{3+}), holmium (Ho^{3+}) or thulium (Tm^{3+}) activator ions) enable a sorting criterion which is independent of the properties of the packaging materials. The authors propose to use up-conversion fluorescence as a unique mean for polymer marking and product identification. To this end, PE-HD film samples, with 10, 100 and 1000 ppm of marker concentration in different polymer matrix colours (semi-transparent, yellow, green, and black) were irradiated with 980 nm diode laser radiation, with an excitation intensity up to 10 W/cm^2. The performance of three different marker types with their maximum emission in green, red, and NIR was measured and assessed both with and without polymer matrix. Moreover, PE-HD sample bottles with tracers were tested, and a tracer regime for specific code generation for improved polymer identification is proposed.

1. Introduction

Plastic waste is an important contributor to global solid waste generation (Singh et al., 2017). Mismanaged plastic waste enters the environment and contaminates soil, water bodies and eventually the oceans (Coelho et al., 2011). Currently about 360 million tons of plastic are produced globally per annum. An average waste mismanagement rate of about 68% can be assumed, with a plastic share in waste of 11%. Consequently, in the coastal regions alone this leads to a global mismanaged plastic mass of 31.9 million tons, and to about 5 to 13 million tons entering the ocean (Jambeck et al., 2015).

The 2015 European action plan for the Circular Economy (European Commission, 2015) addresses plastics as one of five priority areas. Based on this action plan, in 2018 a European Strategy for Plastics in a Circular Economy (European Commission, 2018) was published, to promote a “new plastics economy”. Key elements of this economy comprise the development and use of sustainable materials, the adoption of reuse, repair, and recycling options in plastic and plastic product design and production. As of today, the most important sector for polymer applications is packaging. Although polymers only rank second in packaging material waste generation behind paper/cardboard, packaging is the most important single sector for polymer application in Europe. The total plastic converter demand in the EU (EU28 + NO/CH) in 2017 was 51.2 million tons, out of which 39.7% were used for packaging alone (Plastics Europe, 2019), as shown in Table 1. Regarding the resin types addressed, the most important applications of all polyolefins (PP, PE) along with PET are in packaging (Plastics Europe, 2019). Moreover 2016 data show that 61.6% of all post-consumer plastic waste collected originates from packaging (Plastics Europe 2018). On the other hand, the total (materials) recycling share only reaches 31.1% of all plastic waste collected, while the share of plastic packaging recycling is slightly higher with 40.9%, or 6.8 million tons in 2016 (Table 2).

In Germany, starting January 1st, 2022, a plastic packaging

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Table 1
EU28 + NO/CH Plastics converter demand in 2017 (total 51.2 million tons) (Plastics Europe, 2019).

EU Industry sector	mass share [%]
Packaging	39.7
Building & Construction	19.8
Automotive	10.1
Electrical & Electronic	6.2
Household, Leisure & Sports	4.2
Agriculture	3.4
Others	16.7

Table 2
EU28 + NO/CH Plastics waste collection and recycling (Plastics Europe, 2018) (Plastics Europe, 2019).

	2016 [%]	2016 [mio t]
Total plastic post-consumer waste collected		
Recycling total	31.1	8.4
Recycling in EU [% of recycling total]	63	5.3
Recycling outside EU [% of recycling total]	37	3.1
Energy recovery	41.6	11.3
Landfill	27.3	7.4
Sum	100	27.1
Plastic Packaging post-consumer waste collected		
Recycling	40.9	6.8
Energy recovery	38.8	6.5
Landfill	20.3	3.4
Sum	100	16.7

recycling rate of 63% has to be met (Gesetz über das Inverkehrbringen, 2017). Although to date, lower recycling rates were met in recent years, this new recycling target puts pressure on the entire waste management chain (Gasde et al., 2019): Collection, sorting and recycling technologies have to be modified, along with markets, and packaging design.

Identification and sorting of plastic packaging materials as of today focus on spectroscopic materials properties (Arenas-Vivo et al., 2017), namely based on sensor-based near-infrared (NIR) sorting as a standard (Ahmad, 2004). In state-of-the-art sorting plants the mixed packaging material is pre-sorted according to geometries, and the proper material identification achieved via NIR identification technology (Günther, 2018). This approach is feasible for numerous separation tasks. NIR uses material inherent properties for identification, but unfortunately it is not capable of identifying inner material layers like in multilayer products. Black polymers still pose a problem in NIR identification, too. Moreover, information about the filling of the packaging cannot be obtained with current technology, and wet, dirty, or painted plastic waste surfaces suppress proper NIR polymer identification (Bezati et al., 2010). Moreover, polymers with similar molecular structure like ABS and ABS/PC or SAN (Styrene acrylonitrile resin) may not be identified by NIR with a sufficiently high confidence index (Maris et al., 2012). As a result, for future challenges current NIR sorting technology needs to be improved, supported or replaced by other means for fast, high-throughput sorting in order to comply with economic constraints, and to achieve high quality (high purity) recovered materials.

The shortcomings of current sorting and recycling technology may be overcome with the application of fluorescent marker materials for identification of post-consumer plastic packaging (Arenas-Vivo et al., 2017). These marker materials are providing identification and sorting options independently from the packaging materials properties such as colour, or multi material mixtures, and thus may be used to separate selected recyclable or incompatible materials in the recycling process. On the other hand, research on chemical marker substance interaction with the polymer matrix is necessary to assess ageing and other potential detrimental marker effects. (Maris et al., 2012) stated that for tracer application in polymers a solution on a European level would be required, and that the challenge was clearly more a regulatory than a technological one, as marker application on a large scale requires international standardisation. They mapped a strategy for tracer application at industrial scale, which still lacks implementation as of today.

1.1. State of the art and research and development needs

Fluorescent marker substances application for packaging and other polymer materials has been under research since some decades now (Brunner et al., 2015). A wide range of substances that can be excited with ultraviolet (UV) or NIR light, or even X-rays has been tested, with each exhibiting either single or multiple emission peaks (Bezati et al., 2011). Key physical markers properties are specific absorption and emission properties regarding the wavelengths and also the photoluminescence (PL) decay time. Rare earth element complex substances (for example, europium and terbium based) or organic molecules exhibit these properties (Bezati et al., 2011, Brunner et al., 2015, Kuritka, 2020), so for visible-emitting (VIS) applications they are applied typically between 0.5 and 20 ppm, in case of UV markers 25 to 100 ppm, and for X-ray excitable markers 100 – 1000 ppm (Dvorak et al., 2011). Table 3 gives an overview on fluorescent tracer applications for polymer identification in literature.

The fluorescence of a tracer substance in a polymer matrix is dependent both on the tracer and the polymer matrix fluorescence spectra (Maris et al., 2012). The polymer fluorescence is mainly due to C=C double bonds, but it is also influenced by additives such as fillers, or colorants including carbon black. Nonetheless some research recommended to apply marker substances to sort waste polymers from the automotive and electronics sector with a 40 % (w/w) share of black plastics, typically stemming from shredding facilities. These polymer mixtures are hard to separate by density separation due to overlapping densities of PP, PE-HD, PP filled with talcum, HIPS, and ABS (Maris et al., 2012). As an alternative for fluorescent polymer marking, e. g. magnetic markers might be used. (Brunner et al., 2015).

Single marker substances might be combined in order to generate multiple binary codes from a limited number of substances (Ahmad, 2004), making it possible e. g. to generate seven codes (2^3-1) from three substances only (Bezati et al., 2010). Theoretical work (Bezati et al., 2011) was able to demonstrate that for marking of 1 million tonnes of polymers used for electrical/electronical products and automotive applications a mere 400 t of marker substances in Europe would be necessary if applied at a concentration of 100 ppm.

Marker substances may be used either as additive in compounding, or as a coating, or in ink for label printing. To ensure fluorescent properties during the entire life time of a packaging product, PET coatings have been discussed to be feasible, and for PE-HD the fluorescent materials application as additive is recommended: Research targeted to PE-HD containers from waste packaging used about 10 ppm organic tracer substances (Quinacridone pigments and rhodamine-6G) excitable by UV and emitting in the visible spectrum, with little overlap of UV fluorescence of the tracers with commercial polymers' fluorescence, although literature data on polymer fluorescence might be drastically different to waste polymer sample emission behaviour. Accelerated ageing was performed by elevated temperature (80 °C), immersion in deionized water, and UV exposure of the samples. Results showed on the one hand broad fluorescence signals (minimal peak width about 40 nm), no significant change of polymer structure, but also a clear signal intensity decrease in all cases of accelerated ageing was observed. Nonetheless, after all thermal, hydrothermal, and photochemical stresses still a detectable fluorescence was obtained. (Arenas-Vivo et al., 2017). Besides organic phosphors, some inorganic tracer materials such as lanthanide-based or zinc-based complexes are offering advantageous chemofluorescent properties (Maris et al., 2012): Rare earth materials(Y, Ce, Nd, Gd, Dy, Er, Yb) in polypropylene were tested using X-ray fluorescence, with concentrations between 0.1 and

0.01 % (w/w). Twin screw extrusion and injection moulding were used for sample preparation, and a later SEM imaging showed a homogeneous tracer dispersion and no aggregates. X-ray measurement time was 1 min, and minimum concentration of 0.1 % (w/w) proved to be necessary for sample identification, although compared with UV (surface) analysis, X-ray analysis is a volume detection process reaching up to 1 mm into the samples' volume. In these experiments, PP melting and crystallization behaviour remained unchanged, although mechanical properties were affected, resulting in a slightly increased Young's modulus. (Bezati et al., 2010).

If using lanthanide or zinc oxide compounds in PP or ABS in concentrations between 25 and 250 ppm, no influence on the mechanical properties of the samples by adding the tracers has been observed: Material properties of ABS did not change as long as the marker concentration stayed below 250 ppm (Brunner et al., 2015). Ageing amongst others by thermal, UV and water immersion treatment was tested and showed different effects, i. e. an increased signal intensity with PP (which was whitened due to ageing), and a weaker signal with ABS (which tended to become yellow), which might be attributed to the change of the samples' surface properties (Maris et al., 2012). Moreover, photo-degradation experiments with PP filled with 1000 ppm marker in UV did not yield any marker-driven effects (Bezati et al., 2011).

Besides their use as tracers, up-conversion phosphors have also been discussed as a means for catalytic contaminant degradation in aqueous media (Zhong et al., 2019), or to produce antimicrobial effects, using mainly low (non-laser) excitation conditions, although (Sahu et al., 2018) question the photocatalytic effect by up-conversion emission from visible light excitation and attribute it to merely chemical (not optical) effects. Up-conversion emission is assessed to be in the µW/cm^2 range with peak e. g. solar irradiation used for excitation at around 100 mW/cm^2 (Sahu et al., 2018). In contrast to this, IR (980 nm) to UVA up-conversion is known to be orders of magnitude more efficient than VIS to UV up-conversion (Sahu et al., 2018).

Target marker based sorting products as of today have been entire products, or merely ground polymer particles, while the latter have been sorted by automated identification and sorting processes (belt speed up to 3.5 m/sec, reaching a 95% sorting purity with 0.5 to 5 ppm marker concentrations (Ahmad, 2004)). Also ground technical polymers such as POM, PBT, ASA were identified on the basis of four different marker substances and sorted in a laboratory-scale sorting device with a throughput of up to 300 kg/h and purities beyond 99% (Brunner et al., 2015) with both VIS emission and excitation signals. The challenge of autofluorescence (and hence disadvantageous signal-to-noise ratio) can be overcome when up-conversion markers are used, which are excited with NIR irradiation (at 980 nm), and emit their signal in the VIS or NIR spectrum. If applied in a dark environment, only the emission from the fluorescent marker and no polymer autofluorescence is visible.

Inorganic marker substances with particle sizes down to approx 5 µm (Gao et al., 2017) may be used in polymer processing and printing processes like standard filler or pigment substances. Marking both of the packaging material itself or the label is possible (Fig. 1), but also any other auxiliary material of the package (printing ink, glue) may be equipped with marker substances. Selection criteria for the place of application include material efficiency (total mass of marker substance required to properly identify the packaging material), marker separability (marker substance should be separated from the recycled polymer packaging material) and technological compatibility (minimal adaptation requirements to current processes in the packaging chain). Table 4 gives a qualitative, relative assessment of miscellaneous marker application options in or on the packaging solutions.

1.2. Up-conversion photoluminescence effects for marking

The marking of objects with photoluminescence marker substances

Table 3
Overview on published research on fluorescent tracer applications for polymer identification.

Reference	Tracer type	Fluorescence (detection) wavelengths	Excitation wavelengths	Polymer matrix applied	Additional information
(Arenas-Vivo et al., 2017)	Organic	VIS	UV	PE-HD	Concentration 10 ppm, work included ageing
(Brunner et al., 2015)	n/a	VIS	VIS (blue)	POM, PBT, ASA	Concentration (sub)ppm level
(Langhals et al., 2013)	Organic	VIS	VIS	POM	Concentration below 0.1 ppm, 20 ppm in black polymer
(Maris et al., 2012)	Inorganic	VIS	UV	PP, ABS	25-250 ppm
(Bezati et al., 2010) (Bezati et al., 2011)	Inorganic	7-60 keV	X-ray	PP	Concentration 0.1 – 0.01 ppm
(Ahmad, 2004)	n/a	VIS	UV	PE-HD, PE-LD, PP, EVA, PVC, PET	Concentration 0.5 – 20 ppm, work included ageing

n/a = not available, VIS = visible light, NIR = near infrared irradiation, UV = ultraviolet irradiation

Fig. 1. Application of up-conversion-based fluorescent markers on labels (left bottle, and enlarged inset image) as well as in the packaging material (right bottle, center) (photo: Polysecure GmbH).

is usually based on the downshifting physical effect (Stokes fluorescence): The new emitted photon has a lower energy than the absorbed one, the difference in energy is absorbed by the marker crystal in the form of vibrational energy (phonons). It does not matter if the excitation of the marker particles happens in the UV, VIS or NIR range, the emitted photons always have a smaller energy (longer wavelength) than the absorbed photons.

In contrast to that, in the "up-conversion" effect (anti-Stokes-fluorescence) the emitted photon has more energy (a shorter wavelength) than the absorbed photon. It is a two-step process where two photons are added and a photon with higher energy can be emitted. In Fig. 2 the effects of downshifting (a) and up-conversion (b) are depicted schematically. In up-conversion, two photons are absorbed via an intermediate energetic state (E1) during up-conversion (UC), and an overall higher energetic state (E2) will be achieved. Eventually, only one photon with higher energy will be emitted. Up-conversion markers are e. g. excited with NIR light (980 nm) and then produce visible or NIR light (Fig. 3).

Usually, for synthesis of up-conversion materials inorganic crystals (host materials) are co-doped with ions of rare-earth elements. In the present case, a host oxide crystal doped with sensitizer ions (ytterbium, Yb^{3+}) is used in combination with activator ions of either erbium (Er^{3+}), holmium (Ho^{3+}) or thulium (Tm^{3+}). The ytterbium (Yb^{3+}) has a high probability of absorbing a photon and can then pass them to the activator ions via energy transfer processes. This combination results in a better absorption of the incoming light and thus ultimately emit more up-conversion light.

Up-conversion and down-shifting can also take place within the markers in parallel. However, the up-conversion is a unique process, resulting in emission happenning in a wavelength range free from both (downshifted) polymer autofluorescence and luminescence of contaminants. This guarantees detection of the markers with versatile photodetectors with a high signal to noise ratio.

2. Experimental setup

Selected polymer products (film and blow moulded products made from PE-HD) were used in optical measurements (Fig. 4). The film samples were extruded with conventional blow molding HDPE, with 10, 100 and 1000 ppm of marker substances. The samples were irradiated with 980 nm diode laser radiation (L980P200, Thorlabs Inc.). The laser beam was additionally focused to increase the excitation intensity up to 10 W/cm^2 (on the samples' surface). UC emission was collected by short-focus lens and coupled into the optical fiber (M59L01, Thorlabs Inc.), connected to the highly sensitive irradiance calibrated CCD spectrometer (AvaSpec-ULS2048 × 64-TEC, Avantes). The scattered and reflected excitation light was rejected using dichroic short pass filter (FF01-950/SP-25, Semrock).

3. Results of markers in coloured plastics

Fig. 5 displays up-conversion spectra of the Yb^{3+}/Er^{3+} -based marker dispersed within semi-transparent plastic films. The up-conversion spectra demonstrate characteristic peaks of Er^{3+} emission at 540 and 670 nm. All investigated plastics possess only weak NIR absorption ($\lambda > 900$ nm) – see Fig. 6a. Thus, up-conversion markers dispersed in the polymer films with different colour pigments can be equally excited with 980 nm laser. However, the pigments can differently absorb emitted photons effecting on detected intensity of up-conversion photoluminescence (PL). The yellow semi-transparent

Table 4
Relative assessment of marker substance application in different elements of packaging solutions.

Application of marker in	Marker material efficiency	Marker separability	Technological compatibility	Comment
Packaging material	Medium to low, dependent on the translucence of packaging material and label / artwork	Low, as marker becomes part of polymer compound	High, as marker can be included in masterbatch	Grinding does not change material identification properties
Label – base materials	Medium, dependent on translucence of artwork on label	High, as labels removal is standard in recycling processes	Medium-high, depending on label material	Packaging loses marking along with label removal
Label – print	High, as only a small surface area needs to be marked	High, as label removal is standard in recycling processes	Medium, as printing solution for marker particles is under development	Packaging loses marking along with label removal
Direct printing on packaging	High, as only a small surface area needs to be marked	Medium, as direct print removal has to be applied	Medium, as printing solution for marker particles is under development	Most packaging material loses marking when package is ground
Label – glue	Medium, dependent on translucence of artwork on label	High, as label removal is standard in recycling processes	High, as marker can be included in glue formulation	Compatible only with a limited number of label solutions, marker visibility may me impaired by label material

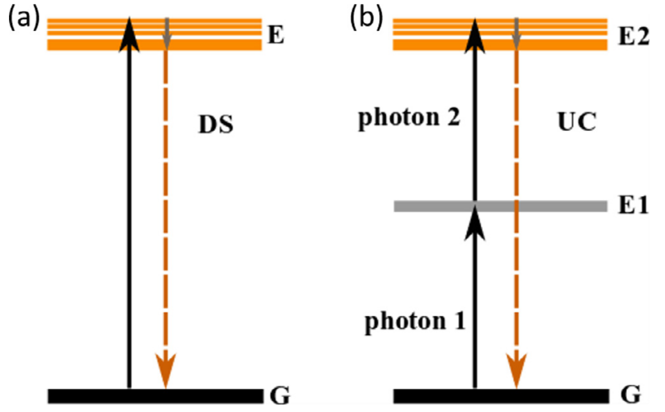

Fig. 2. Basic luminescence mechanisms: a) Down-shifting or Stokes emission: the material gets excited into the higher state “E”, loses some energy into vibration and emits a photon with less energy; b) Up-conversion: two photons are absorbed and the material goes into the higher states E1 and then E2. There it loses some energy into vibration and then emits a photon with higher energy than one of the absorbed photons.

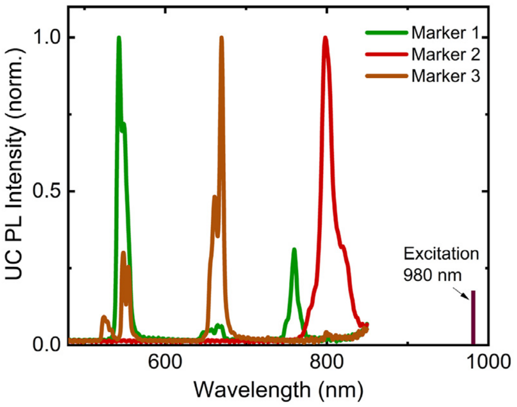

Fig. 3. Emission spectra of selected marker materials, laser excitation at 980 nm.

plastic demonstrates strong absorption at $\lambda < 500$ nm (see Fig. 6a) and, thus, has very minor influence on up-conversion signal (Fig. 6a) (similar with the white semi-transparent plastic). The maximal intensity of the up-conversion signal for green, red and NIR peaks is foreseen in this case. On the other hand, Fig. 5b and 5c indicate that green and red pigments modify the emission of the markers. The red pigment demonstrates absorption at $\lambda < 600$ nm (Fig. 6a). Therefore, strong reduction of the green emission peak is expected. Indeed, Fig. 6 displays an approximate hundredfold decrease of green peak intensity and only a minor decrease of red peak intensity for the red semi-transparent plastic as compared with the yellow plastic. Contrarily, when the marker is dispersed in the green semi-transparent plastic (with broad absorption band between 600 and 800 nm, see Fig. 6a), the strong reduction of red peak intensity is observed (Fig. 6b). These results describing the effect of plastic colour are additionally summarized in the Fig. 6b. Here a normalization of up-conversion intensity (measured for the plastics with 1000 ppm concentration of the marker) is used. The Fig. 6b clearly indicates that the Marker 1 (Fig. 3) is not suitable for labelling of the red plastic, whereas the Marker 2 is not suitable for labelling of the green plastics.

In case of Yb^{3+}/Er^{3+} -based marker dispersed in black partially transparent plastic the up-conversion luminescence can be only detected at concentrations > 100 ppm with significantly reduced strength of the signal (Fig. 5d). A black pigment with absorption over all visible/NIR spectrum is a well-known problem for plastic sorting (Ragaert et al., 2017). Neither existing NIR-sorting nor marker based

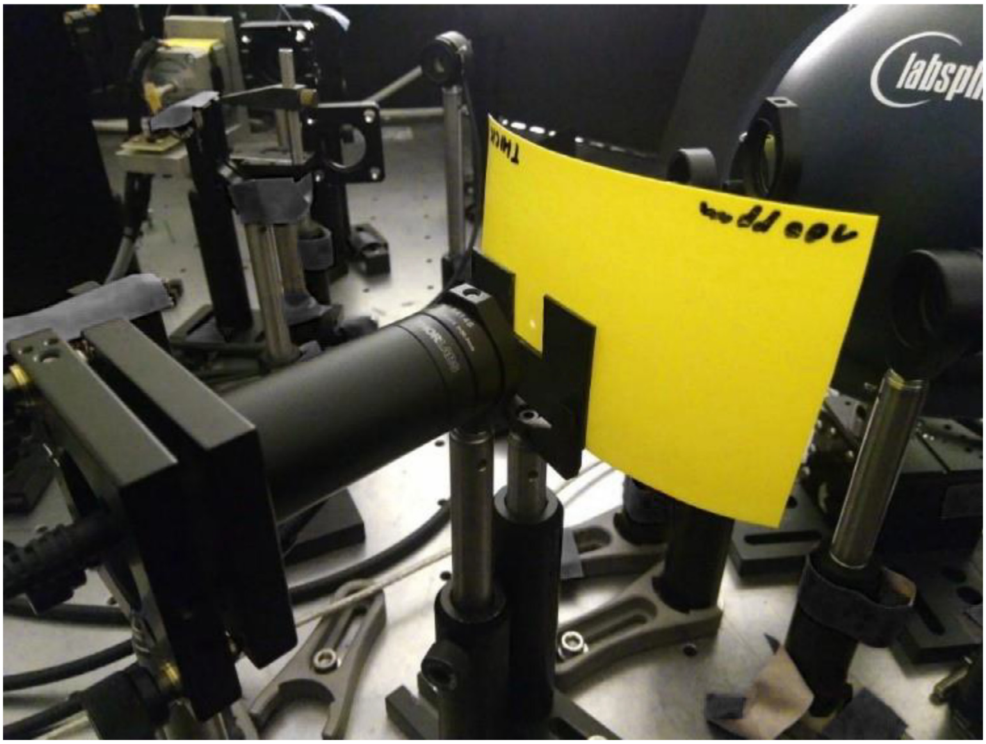

Fig. 4. Optical measurements of PE-HD film sample with 980 nm laser excitation (photo: IMT - KIT).

sorting can efficiently help to sort out black plastic in this case. However, new black pigments not absorbing NIR photons are available since recently on the market (Becker, 2017). We assume that plastics with such pigments can be identified when the NIR up-conversion marker 3 (based on Yb^{3+}/Tm^{3+} pair of ions) emitting at 800 nm (Fig. 6) is applied. In general, NIR the (Yb^{3+}/Tm^{3+} - doped) is very prospective and can be used for labelling of plastics without strong plastic colour interference.

The aforementioned semi-transparent polymer films represent a strategy when the up-conversion luminescent markers are embedded into bottle sleeves or printed directly on surface of a bottle. In the optimal case, all markers can be mixed with white or yellow pigments without any restrictions. There are also no limitations to mix the NIR marker 3 (Fig. 3) with colour pigments, with one exception – black pigment. Green and red pigments should be used with caution as these pigments can significantly reduce the strength of up-conversion luminescence.

Within the next step of our investigation, another strategy was evaluated. Non-transparent plastic bottles of three colours (white, green and black; Fig. 7a) were produced using Yb^{3+}/Er^{3+} - based marker. The marker was first added to a masterbatch via extrusion, and subsequently this masterbatch was added to the polyethylene in blow moulding. The up-conversion emission was measured in five different points of the bottles and standard deviation of UC emission intensity (Sd) was calculated (Table 5).

The highest intensity of up-conversion emission (Fig. 7b) corresponds to the white bottle and the Sd doesn´t exceed 4 % when the marker concentration is only 100 ppm. It indicates that the marker is distributed quite homogeneously without zones with increased or decreased concentration of the marker. Increase of the marker concentration leads to even stronger reduce of Sd down to 1.5 %. The strength of green and red peaks of up-conversion luminescence decreases when the marker is used in the green bottle. The up-conversion signal reduced by approximately ten times demonstrates one important limit of utilizing red and green UC emission in case when the marker is added directly to the polymer material. This limit is more pronounced for black bottles which were tested as well: The UC PL was not detected even for the highest marker concentration – 1000 ppm. The problem of black plastic sorting, thus, can be solved only via using new black pigments with NIR transparency together with the NIR up-conversion marker (Yb^{3+}/Tm^{3+} - doped) exploiting NIR excitation (980 nm) and NIR emission (800 nm).

By mixing the markers it is possible to build a code system. For this purpose, tests were carried out with 100 -500 µg/cm^2 markers embedded in commercial white acrylic paint as supporting material. Lab scale screening tests using markers with “25%” combinations discussed below showed clear signals which enable sorting in a technical environment. For the tests a 980 nm laser with 4.5 W/cm^2 (45 mW/mm^2) along with a photodiode at a distance of 300 mm to the sample and no further optics was used.

The marked area of only 1 cm^2 is sufficient to perform the measurement. The code system is designed in a way that the total amount of markers does not exceed 100 µg/cm^2. For example, 50% Marker1 + 25% Marker2 + 25% Marker3 would be a possible combination, and the smallest colour peak to be measured would be for the marker with 25% portion. Minimization of this smallest amount - in the example mentioned it was 25% - will yield an increased number of possible combinations. The current development goal is to reach a 12.5% share of marker, which would result in 45 possible combinations.

4. Summary and outlook

Plastics recycling is in the focus of sustainability policy of the European Union. While more than about 50 million tons of plastics are converted in the Europe, approximately 40% of this material is used for packaging only. This puts the packaging industry in the focus for innovative plastic waste management approaches. Current plastic packaging sorting technology uses NIR spectroscopy as a key technology for materials identification and separation, and further increase of recycling rates along with higher quality requirements (e. g. food grade qualities) is demanding new approaches. Marker based sorting

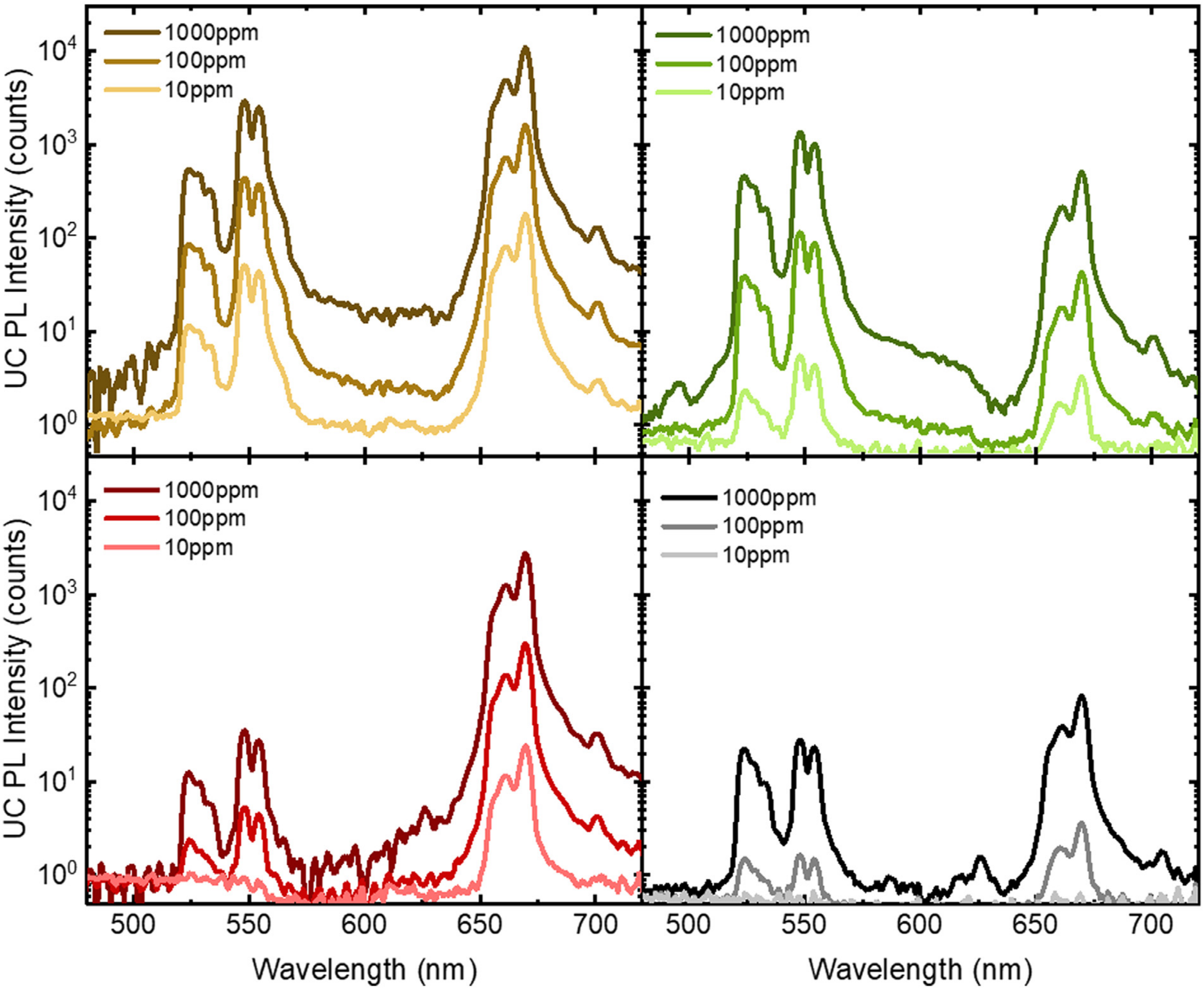

Fig. 5. UC PL spectra of semi-transparent coloured plastics ((a) – yellow, (b) – green, (c) – red, and (d) - black) labelled with different concentrations of Yb^{3+}/Er^{3+} - based marker. Excitation wavelength 980 nm. Excitation intensity 10 W/cm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

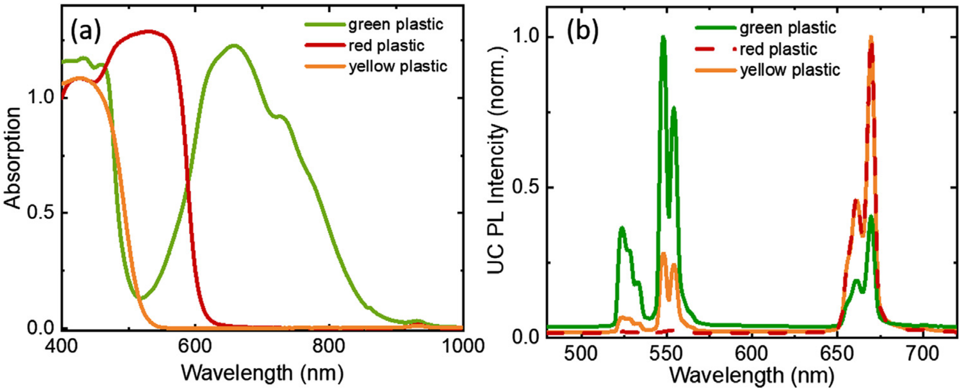

Fig. 6. (a) Absorption spectra of semi-transparent plastics used as the polymer host material for PL markers; (b) normalized UC PL measured for concentration Yb^{3+}/Er^{3+} - based marker of 1000 ppm. Excitation wavelength 980 nm. Excitation intensity 10 W/cm^2.

may provide such a new approach, using man-made substances and relying on the anti-Stokes fluorescence or up-conversion effect.

Research work presented here uses NIR excitation for generation of visible light photoluminescence (light emission) from rare-earth based marker substances. Minimum three emission lines from individual marker substances are available, which emit in green, red and in the infrared.

Marker photoluminescence performance of one of these substances in miscellaneous polymer matrix material was tested, applying marker concentrations in the polymer (PE-HD) between 10 and 1000 ppm, and using different matrix colours. The geometries tested were both extruded polymer films and blow moulded polymer bottles. Measurements show a good homogeneity of the marker substance in the blow moulded parts. Moreover, they exhibit good to reasonable emissions if used in white, green or yellow matrix material, but unsatisfactory results in black polymers.

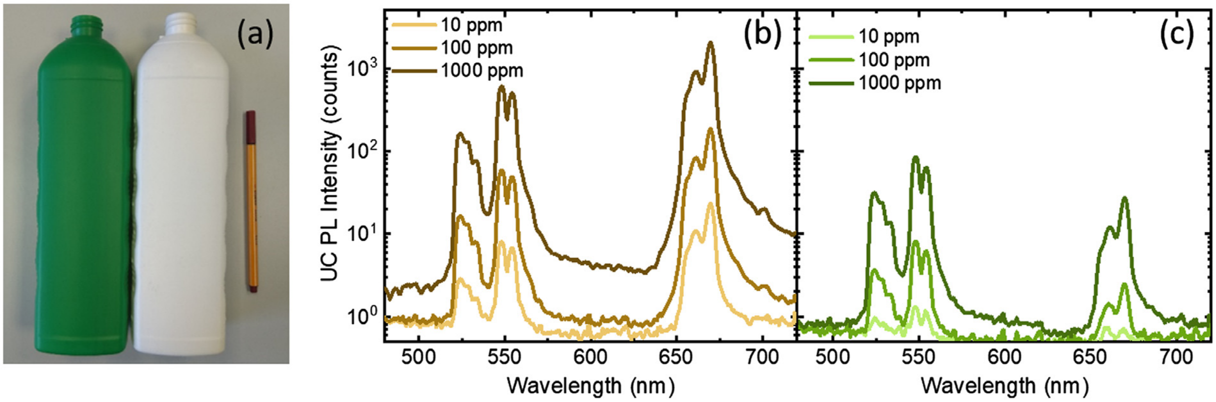

Fig. 7. (a) Example of coloured plastic (PE-HD) bottles labelled with the Yb^{3+}/Er^{3+} - based marker; UC PL spectra of coloured plastic bottles ((b) – white and (c) – green) labelled with different concentration of Yb^{3+}/Er^{3+} - based marker. Excitation – 980 nm. Excitation intensity 10 W/cm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5
Standard deviation (S_d) of UC PL measured for coloured plastic bottles with different concentration of the Yb^{3+}/Er^{3+} - based marker.

Sample	S_d for peak λ_{em} = 550 nm, %	S_d for peak λ_{em} = 670 nm, %
White (10 ppm)	10	8.5
White (100 ppm)	4	3.5
White (1000 ppm)	1.5	1
Green (10 ppm)	No emission	No emission
Green (100 ppm)	2	6.5
Green (1000 ppm)	2	5
Black (1000 ppm)	No emission	No emission

The results of this research show that fluorescent markers can contribute to solving the sorting challenge of waste streams. Regarding post-consumer packaging recycling, undefined wastes have to be sorted, which are by principle not sortable with sufficient quality and into the really needed fractions using their intrinsic properties only. Examples include the identification of food grade material from PET or polyolefin packaging, or of specific polymer types. The core question is: How much of the fluorescent marker substance has to be integrated in the packaging items in order to provide reliable and quick identification?

Regarding the use of up-conversion fluorescence, we have shown that 100 – 500 µg of up-conversion marker per packaging item are sufficient to read sorting codes based on the up-conversion spectrum of the markers. Our development further proofed that due to the anti-Stokes shift of emission at upconversion, one can rely that there is no (downshifted) background emission from plastics and additives in the relevant wavelength range generated by the NIR excitation. We have shown how this unique advantage can be used to generate clear signals of the marker in complete absence of any signal by the packaging itself.

Our development now diverts into the tracer-based sorting (TBS) options “TBS complete” and “TBS light”. “TBS complete” is a new sorting process with singulation, TBS detection and precise sorting into fractions which is the most cost-efficient concept to better sort and thus yield much higher recycling rates for packaging waste worldwide. “TBS light” in contrast relies on the existing state of the art waste sorting process by which the waste items are not singulated and thus a waste stream is always diverted into two output streams. Maximum recycling rates for plastic packaging today, employing the best possible state of the art technology, ranges at 30%. Tracer based sorting is a new sorting technology which along with proper design for recycling can increase recycling rates up to 60-80%. This large step towards a circular economy for plastics would also save very large amounts of greenhouse gas emissions. In general, our research and development has shown that marker-based sorting has a great potential for the sorting of many other waste streams and thus for circular economy in general.

Author contributions

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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