Removable Identification Technology to Differentiate Food Contact PET in Mixed Waste Streams: Interim Report

Authors

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Executive Summary

The equivalent of 66 billion 1.5 L poly(ethylene terephthalate) (PET) bottles were collected and recycled in 2014, representing 57% of bottles and containers placed in the market in Europe (based on a Petcore Europe study). The EC-funded "Polymark" project brings together stakeholders from across the PET value chain with the common aim of increasing the availability of "closed-loop" recycled PET (from used bottle to new bottle) by improving identification and separation of food contact approved PET from mixed waste streams. This interim report outlines the successful development of a prototype, flexible, coating-based approach for marking PET bottles, detailing the combination of suitable food-contact approved fluorescent markers and alkali-strippable polymeric matrices used. Removal of the marker is demonstrated so that post-recycling marker accumulation and associated potential for false positive detection in the long term is minimised. Detector technology suitable for high speed sorting was developed in parallel to marking technology and initial results in this area are also reported.

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Introduction

In 2012, 25 million tonnes of plastic waste were created in the European Union. The fate of this waste was split between recycling (26%), energy recovery (36%) and landfill (38%). Closer inspection of the collected data shows a wide variation on plastics landfill waste between EU members, with Germany sending less than 10% of plastic waste to landfill (due to a landfill ban in 2005) and the UK sending more than 66% of plastic waste to landfill (PlasticsEurope, 2015). Much of this waste constitutes a valuable resource in terms of material reuse, chemical building blocks or (in the worst case) energy recovery. The positive news is that the proportion of plastic waste going to landfill reduces year on year due to improvements in collection schemes and recycling technology, and investment in energy recovery. However, clearly there is still significant room for improvement.

Poly(ethylene terephthalate) (PET) is a key target for further improvements to recycling technology. PET accounted for 6.9% of the total EU plastics demand in 2013 (PlasticsEurope, 2015), with approximately 30% of that arising from single use, food contact bottles (*Figure 1*) (Petcore Europe, 2014). In addition, its thermoplastic nature and chemical stability lend well to recycling processes. The majority of recycled PET (rPET) comes from bottles (food contact and non-food contact) and other packaging derived from thermoformed sheet/injection moulded products since these are the easiest to mark for identification as recyclable. Recycling of PET has been extensively discussed in the literature and therefore will only be discussed in broad terms here (Al-Salem et al., 2009; Awaja and Pavel, 2005; Hopewell et al., 2009; Luijsterburg and Goossens, 2014; Shen et al., 2010; Welle, 2011). It can be subdivided into mechanical systems (where the articles are cleaned, flaked and re-extruded) and chemical systems (where the articles are returned to their original chemical feedstocks to make new, virgin, PET). Key challenges associated with mechanical recycling are; contamination with other polymers (particularly PVC) that cause discolouration and molecular weight reduction caused by thermal degradation that leads to changes in PET properties. Mechanical systems can be further sub-divided into "open loop" systems (where bottles become other, lower value products such as textile fibres) (Shen et al., 2010) and "closed loop" systems (where bottles are turned into new bottles) (Welle, 2011).
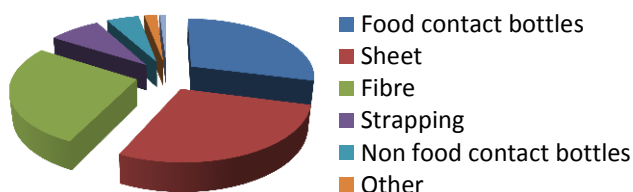

Figure 1. PET end-use market share in 2013 (Petcore Europe, 2014).

The penetration of rPET into the various end use applications is shown in *Figure 2*. Use of rPET in fibre and sheet applications was around 50/50 with virgin PET in 2013, but use of rPET in food contact bottles, while growing slowly, remains low at around 10% with respect to virgin PET. The reasons for this will be discussed shortly, but it is clear that there is a great opportunity to increase rPET use in higher value, blowmoulding applications.
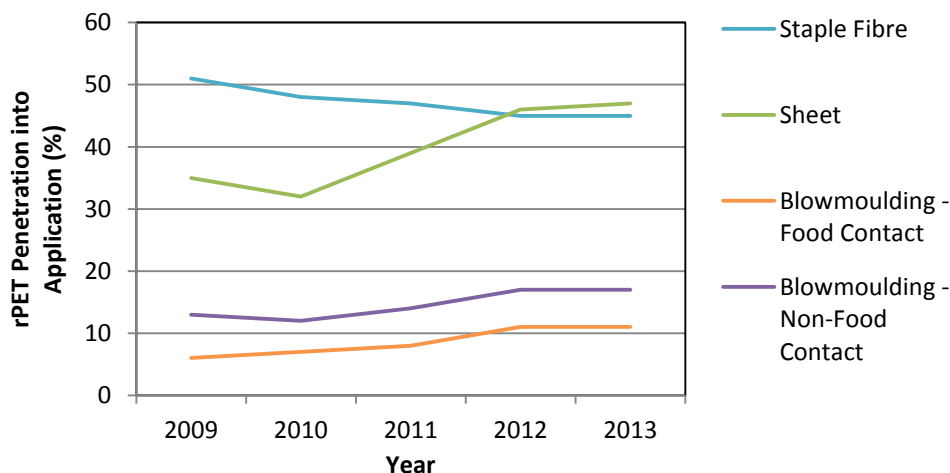
Figure 2. Penetration of rPET into selected end-use applications (Petcore Europe, 2014)*.*

In addition to the recycling challenges already described, to allow fully closed-loop recycling of PET, the process must fulfil the requirements of EC legislation "on recycled plastic materials and articles intended to come into contact with food" (EC, 2008). This legislation seeks to protect consumers from contamination of food-safe plastics during the recycling process: once a food-safe PET bottle goes to the consumer, it may be used to hold alternative (non-food) materials, or it may become contaminated with non-food products/plastics during the collection/recycling process (Welle, 2013). This may be a particular challenge in countries where recycling collections are of mixed waste, or could arise from counterfeit materials (Puype et al., 2015). An important exemption to the regulation is for recycled plastics used behind a "functional barrier" (subject to migration testing). Thus, rPET may already be used in food packaging provided it is separated from the food product behind a layer of virgin PET. Such products reduce the demand for virgin polymer, but cannot eliminate it and add complexity to the manufacturing process.

The following points are key to the European Food Standards Agency (EFSA) approval of material/articles from a recycling process (EC, 2008):

1. Input material must originate from articles manufactured in accordance with regulations for food contact plastics (EC, 2011, 2006)
2. Either…
   o Input arises from a closed and controlled product loop
   or
   o The recycling process is able to demonstrate reduction of contamination to a concentration that does not pose a risk to human health
3. Existance of an appropriate quality assurance system to ensure reproducibility of the product

Points 2 and 3 can be demonstrated in a straightforward manner using a combination of cleaning processes, vacuum stripping, migration testing, chemical analysis and management system audits (EFSA, 2012a, 2012b; Welle, 2011). However, point 1 is more difficult to achieve where food contact plastics are collected as part of a mixed recycling waste stream. In addition, plastic materials become

steadily more complex as greater shelf-life for package contents is sought through multilayer/ additivated barrier materials and through active packaging: such materials may be labelled as, or identify as PET in current sorting processes, but will lead to poor quality rPET products. The challenge is therefore for sorting and separation of these materials firstly, to meet EFSA requirements and secondly, to ensure the future quality of rPET (Dvorak et al., 2013). Improvements in rPET quality and acceptance of a greater proportion for food contact use should enhance demand for this material and subsequently lead to greater penetration rates of rPET into the food contact bottles market. In principle, up to approximately 20% further reduction in demand for virgin PET (with associated carbon emission reductions (Packham, 2014)) is possible if all produced food contact PET bottles are captured into a fully closed-loop recycling system. In practice, material "leakage" through increasing complexity will make this reduction unachievable unless a practical method is found to manage it (World Economic Forum, 2014). A resolution to the material identification and sorting issue is the portion of the overall picture addressed in this project.

Sorting Techniques

A variety of sorting techniques are currently employed in recycling processes depending on the types of materials to be separated. Sorting may take a manual form (using a combination of operator experience and resin identification codes), or an automated form (using a variety of techniques). Automatic sorting technologies are available using a combination of physical and spectroscopic properties; Brunner and co-workers provide a good introduction to these methods (Brunner et al., 2015). Such automated methods can be made faster than manual sorting, but are a higher cost investment. Flotation can be used to sort high density (e.g. PET, PVC) from low density (e.g. PE, PP) plastics, magnets can remove trace ferrous metal impurities carried over from mixed waste streams, triboelectric systems can distinguish plastics in simple mixtures based on their surface charge carrying characteristics, optical systems can be used to separate coloured from clear plastics and near infra-red (NIR) spectroscopy can rapidly identify different types of plastic (Tachwali et al., 2007). All of these systems have limitations (e.g. detection of black plastics/detection within complex mixtures) and therefore a mixture of approaches is needed in automated sorting to get full separation. For example, a combination of density, colour and NIR spectrum will respectively simplify the waste stream, separate the lower value coloured plastics and separate by plastic type. However, separation of complex, additivated and/or multilayer plastics from simple, easy to recycle ones and particularly separation of food contact plastics from non-food contact ones is not achieveable using the current automated techniques.

Use of Markers

The idea of using markers to assist identification and sorting of plastics is not a new one. An early patent relating to this subject was published by Clay and McGuinness in 1985, using benzoxazole or benzothiazole markers (McGuinness and Clay, 1984). A range of patents have subsequently been published expanding on the technology as instrumentation and marker chemistry have developed (Becker et al., 1994; Hachin and Lambert, 2009; Lambert and Hachin, 2012; Lee, 2013; Luttermann et al., 1993). Concepts such as a plurality of markers, binary coding, use of fluorescence decay in addition to fluorescence wavelength and the use of inorganic as well as organic markers have all been discussed in these patents. Marker-based detection products for use in security and

counterfeit prevention for high value articles may be found using a simple internet search. However, despite the high level of patent activity, no marker-based detection system has yet transitioned into wide spread use in the recycling industry.

Markers as plastics recycling aids have also been widely reported in the scientific literature. Bezati *et al.* reported in 2011 on the selection of X-ray fluorescent tracers for automatic sorting of plastics. The use of rare earth oxides as tracers for plastics from waste electrical items was described: this application was stated to be difficult to sort automatically due to high levels of carbon black (Bezati et al., 2011a). The associated experimental investigation of the effect of tracers on polypropylene (PP) properties was reported in parallel (Bezati et al., 2011b). Maris *et al.* also used rare earth minerals, also in conjunction with PP to aid tracing of carbon black grades from automotive and electrical equipment applications (Maris et al., 2012). A combination approach was reported by Langhals, Zgela and Schlücker, using time constants of autofluorescence of some commercial polymer products (i.e. without additives) for their identification (Langhals et al., 2014). In addition, they added perylene and terrylene-based fluorescent dyes to demonstrate further fine-tuning of marking to enable additional identification of special batches. The same type of markers were used by Brunner, Fomin and Kargel for their recent report on a measurement system prototype for automatic sorting of polymer flake (Brunner et al., 2015). Four markers with well-resolved fluorescence were used at concentrations below 10 ppm in a coding-based approach with 3 different polymers: a "true positive rate" of >99% was reported to be achieved in sorting trials with a belt speed of 260 mm s^{-1}.

All of the previous reports use markers incorporated into the bulk of the plastic. In contrast, Kosior et al. recently reported on the results of a WRAP funded study into the use of fluorescent inks for marking food packaging and sorting (Kosier et al., 2014). Sorting purity as high as 93% was achieved using a mixed PP packaging waste with relatively small fluorescent-labelled areas, but the identities of the markers tested were redacted. The surface marking approach is an advantage for food packaging, since the marker does not then have any contact with the food product and opportunities for migration are minimised. However, the authors identified some shortcomings in their approach, including requirement for improvements to sorting yield and purity that could be achieved by coverage of a larger area of the package and removal of the marker to prevent contamination of the food contact material and prevent marker carry through into non-food contact applications after recycling. Food contact status of the marker was not discussed in the report.

Objectives and Scope

The aim of our project is to develop a marker-based system, suitable for large-scale industrial implementation, to reliably detect and sort food contact PET from a PET bale containing a mixture of food contact and non-food contact packaging. A high proportion of food contact packaging in recycling streams comes in the form of drinks bottles, so these were the chosen items for marking. The envisaged process cycle is shown in *Figure 3*. It was assumed that existing detection and sorting methods (e.g. manual, NIR) would already have been used to separate PET from mixed plastic waste prior to this point, and that the majority of labels and caps would have been removed. Additionally,

marker-based sorting was planned for implementation prior to shredding since sorting after shredding can lead to reduced yields (sorting by air jet typically removes a number of flakes rather than just the flake targeted). The marker was required to be removable, since some food contact PET might end up in non-food contact applications after recycling: a non-removable marker would then be mixed in non-food contact product and might lead to false positive detections in later recycling. A coating-based approach was therefore chosen to minimise contact of the marker with the food product and facilitate its removal (and also allows flexibility for the incorporation of additional markers at a later date). The following requirements were set for the marker and coating:

- Marker
    - Food contact approved and commercially available in bulk
    - High intensity visible fluorescence resulting from UV absorbance at 365 nm
    - Distinguishable from background fluorescence of PET and its additives
    - Minimal effect on article colour
    - Detectable within a 3 ms exposure time (calculated based on speed of conveyer belt and expected detector-to-sorter distance)
    - Sufficient stability for the bottle life cycle (including process conditions, and photobleach resistance)
- Coating
    - Food contact approved
    - Water-based formulation
    - Good adhesion to PET
    - Water and detergent resistant in use
    - Removable at recycling plant, ideally using existing alkaline wash processes

Within this paper we report the selection and development of a marker-containing coating from food contact approved ingredients suitable for application to PET bottles. The removability of the coating under alkaline conditions is demonstrated. The ongoing development of an affordable detection system for high speed sorting is briefly discussed and initial results showing successful detection of marked bottles are shown. More comprehensive sorting trials are in the planning stages and results from these are intended for publication when available.
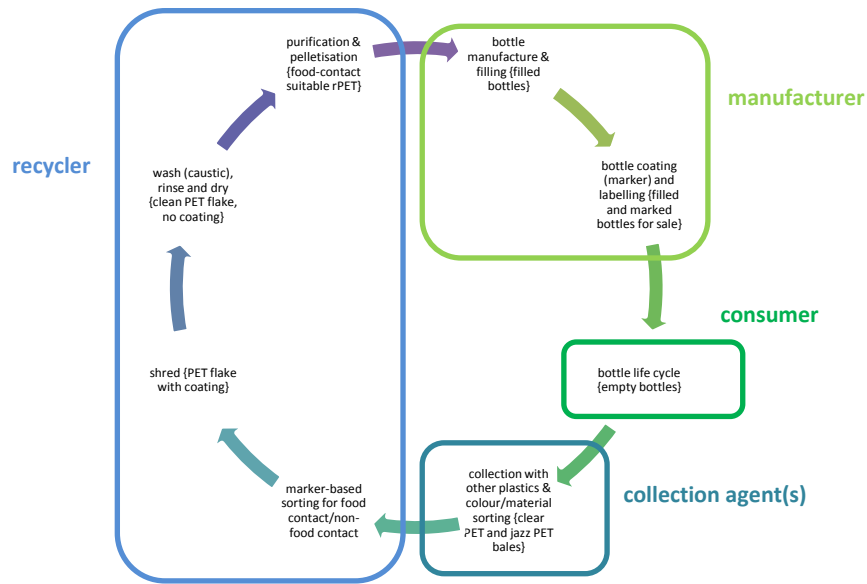
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Figure 3. Target closed-loop process from bottle manufacture to recycling.

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Experimental

Materials

All materials were used as received unless otherwise stated. 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (**M1**) and 4,4'-bis(2-benzoxazolyl)stilbene (**M2**) were obtained from Lambson Ltd; Solsperse 46000 was obtained from Lubrizol (UK); BYK012 defoamer was obtained from BYK (Germany); Neocryl A2092 (DSM) was obtained from IMCD; anthranilamide (≥98%), PEG (BioUltra grade), Tween 80 and sodium hydroxide (NaOH, granules) were obtained from Sigma Aldrich; PET (Equipolymers Lighter C93) bottles for coating and detection trials were supplied by ColorMatrix (Knowsley); PET (PAPET Clear, Lotte Chemical UK) for marker compounding and film extrusion was obtained from Ultrapolymers and dried in a hot air circulating drier at $140^{\circ}C$ for 8 hours prior to use. All water was deionised.

Processing

Marker dispersion: Deionised water (5.63 g) and Solsperse 46000 (0.73 g) were placed in a 100 ml mixing vessel and mixed at 500 rpm for 10 mins. M2 (3.51 g) was added over 15 mins and the speed was gradually increased to 1500 rpm for a further 10 mins. BYK012 (0.05 g) was added and mixed for a further 20 mins at 3000 rpm. Tween 80 (0.20 g) was added and mixed for 10 mins at the same speed. Finally, a further quantity of BYK012 (0.15 g) was added and the speed was reduced to 500 rpm for 5 mins. Pigment was found to settle over time, so the dispersion was stirred prior to further use.

Coating preparation (example, compositions of formulations trialled are shown in Table 1): Deionised water (22.2 g) and PEG$_{400}$ (5.64 g) were stirred with **M2** concentrate (2.92 g). Neocryl A2092 (200 g) was added and stirring continued for a further few minutes. If mixtures were not used immediately, care was taken to rehomogenise by gentle agitation prior to application.

Table 1. Formulation compositions used in spray trials.

Sample ID	Neocryl A2092 (wt%)	Water (wt%)	PEG$_{400}$ (wt%)	Marker dispersion (wt%)
C1	86.7	9.6	2.5	1.2
C2	87.7	9.7	2.5	0.1

Spraying trials were conducted using a Binks M1-G-HVLP gravity fed spray gun equipped with a compressed air feed and held at a fixed distance of 20 cm from the substrate. Bottles were rotated at a speed of 50 rpm during the spraying process. A vertically-oriented fan spray pattern was used with a pressure of 25 psi. Bottles were oven dried at $40^{\circ}C$ for 10 mins after coating.

Coating removal experiments were conducted using simulated "flake" samples of 5-10 mm size. Flake (9.0 g) was added to aqueous sodium hydroxide (50 ml, 2-4 w/v%) at elevated temperature (60-90 $^{\circ}C$) and stirred vigorously for 10 mins. The wash solution was decanted away and the flake was rinsed with hot deionised water (3 x 50 ml), then collected and air dried. Coating removal was

evaluated visually under a UV lamp (365 nm) for residual marker fluorescence and compared to control coated and uncoated samples.

Materials Characterisation

Optical microscopy was carried out using a Motic BA200 microscope equipped with 10x, 40x and 100x objective lenses and a moticam 2300 digital camera directly connected to a laptop. Each objective lens was calibrated using spots of known size to allow measurement of coating thickness following freeze-fracture of specimens.

Colour testing (CIELab coordinates) was performed using a Minolta 3700d spectrophotometer. Results for coated bottles were compared to an uncoated blank bottle prepared from the same PET.

Fluorescence spectra were measured using a portable Ocean Optics USB2000+ spectrometer. Samples were illuminated with 365 nm UV LEDs at 50 cm distance.

Marker Detection System

A benchtop detector system was assembled on an optical table from the following components (*Figure 4*):

- Hamamatsu S-11865-128 silicon photodiode array (128 pixels, 300x600 μm^2 per pixel, 7500 lines s^{-1} readout rate) with detector electronics designed by Sesotec.
- HAMEG instruments external power supply
- Control PC with bespoke software to control detector configuration (exposure time), data display and storage
- Multi-wavelength (UV/visible) LED illumination unit, 2 LEDs per colour (fabricated by Sesotec)
- ZEISS Planar T* 1,4/50 ZF lens with holder constructed by Fraunhofer IPMS
- Long pass filter, cut-off wavelength 450 nm
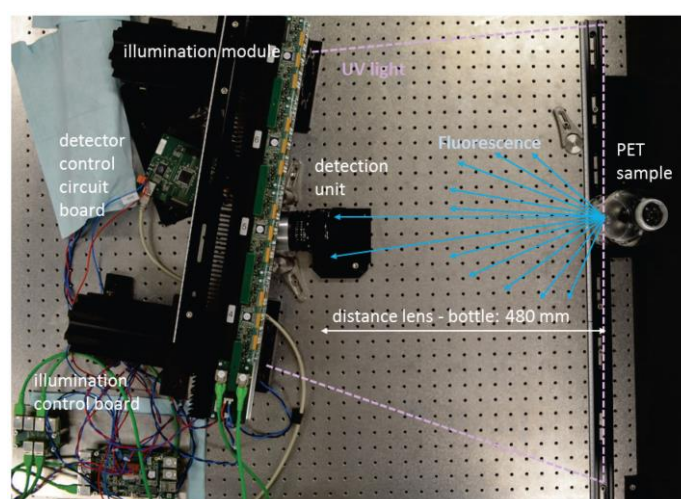- Conveyer belt material as backdrop for samples

Figure 4. Bench-top detection system setup.

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Results and Discussion

Selection and Formulation of Marker

An extensive search of food contact approved "markers" revealed 2 particularly promising candidates with bright fluorescence as well as an important interfering agent: 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (**M1**), 4,4'-bis(2-benzoxazolyl)stilbene (**M2**), and anthranilamide. The latter, has a strong, blue fluorescence and is a typical additive of PET used to scavenge acetaldehyde formed during PET synthesis and processing. Further interference to the marker signal is expected from glues and paper labels containing optical brighteners as shown in *Figure 5*. *Figure 6* shows a comparison of the fluorescence emission spectra from PET, anthranilamide, **M1** and **M2**. The blue emission background from PET (Manikowski and Lijevvski, 2010) and anthranilamide overlap with **M1**, but the peaks of **M1** and particularly **M2** emission are well resolved from these signals. The bright blue background fluorescence can be eliminated by inclusion of an optical filter in the detection system, but such a filter would also interfere with detection of **M1**. Agglomeration of marker pigments and their low surface energy led to difficulties dispersing them into water-based coating formulations. High solids, stable-to-dilution dispersions of both markers were achieved using a combination of hyperdispersant, antifoaming agent and stabiliser, in combination with high shear centrifugal mixing as described in the experimental section.
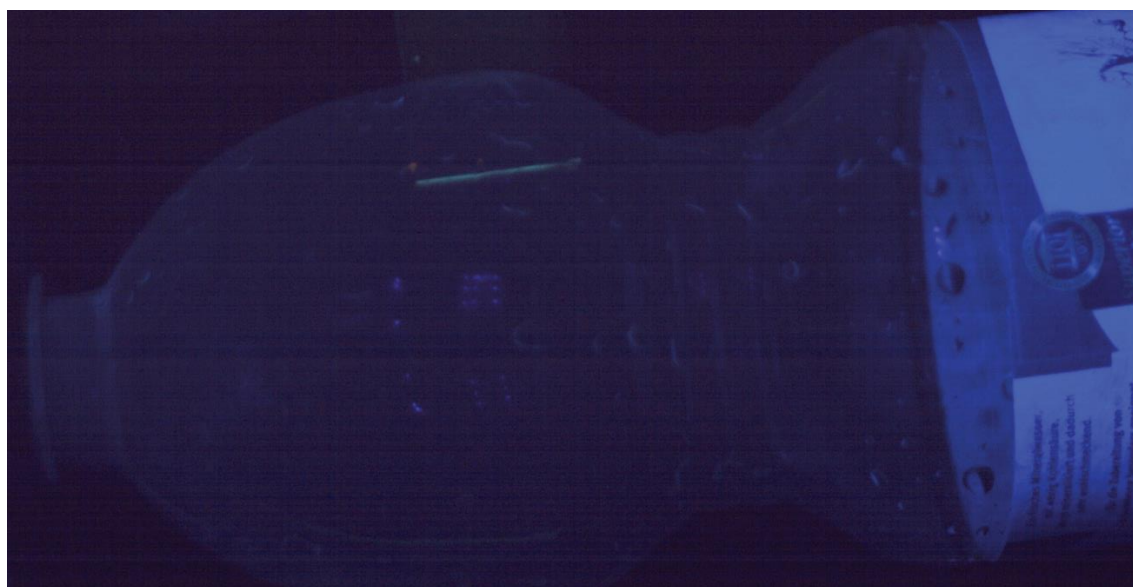

Figure 5. Photograph showing background fluorescence from PET bottle and paper label under UV irradiation at 365 nm.
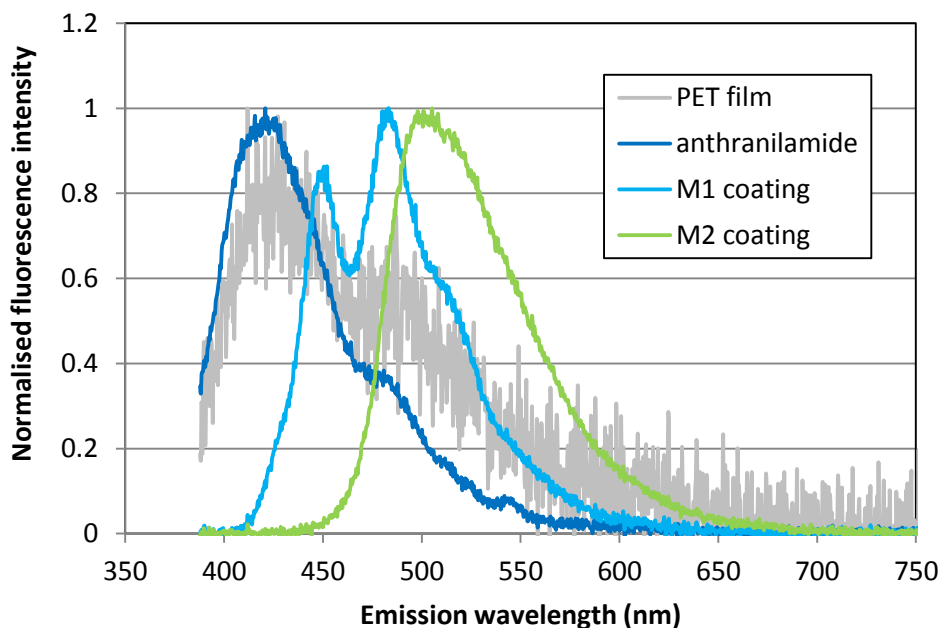
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Figure 6. Normalised fluorescence emission spectra of PET, anthranilamide, M1 and M2. Normalisation allows comparison of the shapes of these fluorescence spectra despite their very different intensity: this overlay demonstrates in particular the similarity between fluorescence spectra of PET and anthranilamide and the different spectra arising from M1 and M2.

Selection and Formulation of Coating

A styrene/acrylic copolymer dispersion was chosen as a proof of concept demonstrator as shown in *Figure 7*. These dispersions contain a copolymer with a proportion of acrylic acid repeat units, typically ionised with a volatile amine base, such as ammonia. On drying, the base is evaporated along with the water, to leave behind a hydrophobic, charge-neutral polymer that can interact with a PET surface through 2 mechanisms: firstly through interaction of electron rich styrene aromatic groups with electron deficient PET aromatic groups, and secondly through hydrogen bonding interactions of acrylic acid repeat units with PET ester groups. On addition to the alkaline wash bath at the end of the recycling process, the polymer will become charged (and water dispersible) again and debond from the PET surface.

A variety of commercial dispersions expected to exhibit this behaviour were qualitatively tested for their film formation, flexibility and adhesion to PET. Neocryl A2092 (DSM) was found to give the best results, although a small quantity of a plasticiser/coalescing agent was still required to aid film formation and coating flexibility. A variety of potential agents from the EFSA positive list were tested, and low molecular weight poly(ethylene glycol) (PEG$_{400}$) was found to give the best combination of film formation and flexibility. Such, low molecular weight, additives have potential for migration leading to changes in coating properties over time. Additionally, the use of a water-soluble additive of this type is expected to reduce water resistance of the dried coating. Therefore ideally, the coating properties would be optimised by adjustment of the copolymer composition so that the use of coalescing agents/plasticisers could be avoided. Alternative dispersion coatings based on different polymer types, but with similar pH responsive behaviour are also available.
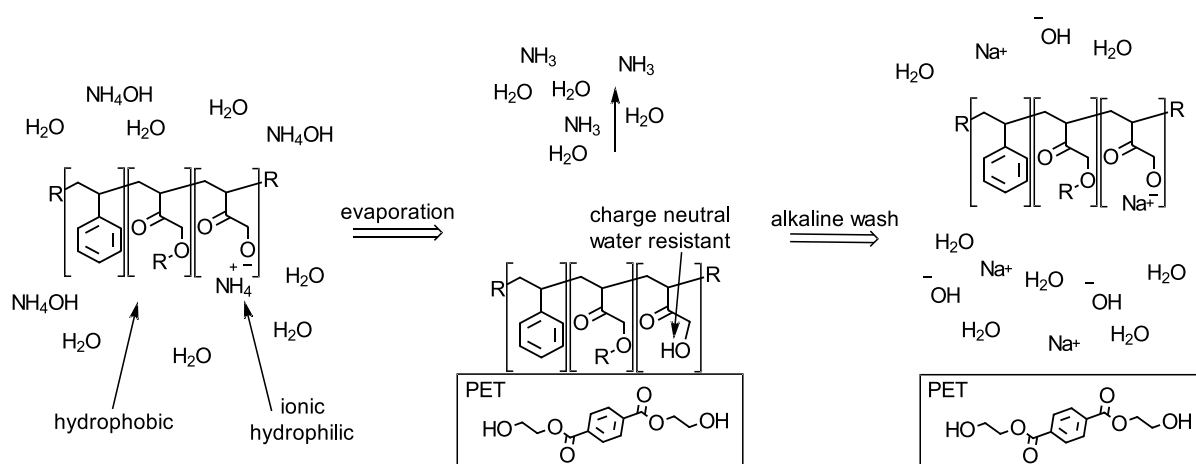
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Figure 7. Commercial-off-the-shelf coating technology based on styrene/acrylic copolymers, exhibiting; water dispersibility in presence of volatile base (left), development of water resistance/adhesion to PET on evaporation of water and ammonia (centre), and debonding/re-dispersion on washing with sodium hydroxide solution (right).

Dilution of the coating formulation was required to adjust the viscosity for optimisation of spray application. Addition of the concentrated marker pigment dispersion was then performed directly: the marker pigment was stable on dilution into the coating, with no coagulation observed by optical microscopy (*Figure 8*). The final coating formulations are listed in the experimental section (*Table 1*). Coating grammage was evaluated from the mass increase and known surface area of the bottles. Samples were cut from various points on the coated bottles, freeze fractured and coating thickness at the fractures was measured using optical microscopy (*Table 2*). It should be noted that spraying was performed manually, therefore variations in coating thickness and uniformity across the bottle are to be expected: industrial scale spraying would be expected to improve coating homogeneity significantly.
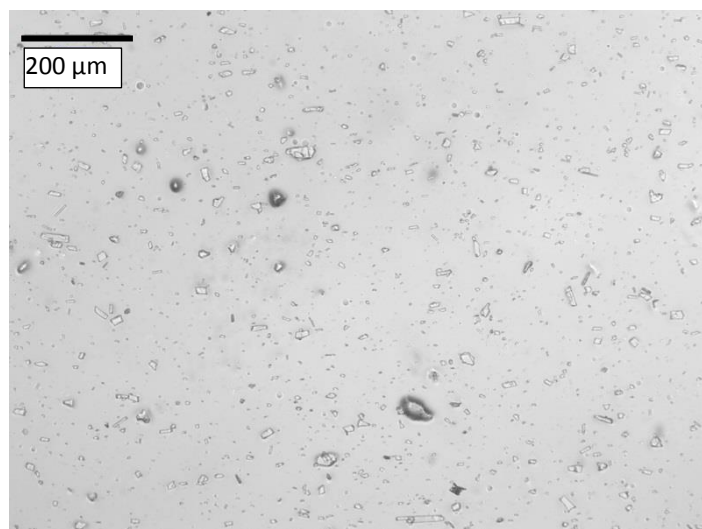
*Figure 8. Typical optical micrograph of coating prepared from formulation **C1** (bar coated onto glass slide) showing **M2** dispersed throughout coating, with no pigment particle agglomeration.*

Table 2. Coating and marker grammage (calculated from mass of coating applied, marker concentration and known surface area of bottle) and thickness (from optical microscopy, average of at least 5 measurements).

Formulation ID	Bottle number	Coating grammage (g m^{-2})	Marker grammage (mg m^{-2})	Coating thickness (µm)
1	13	31.3	313	49.2
2	25	36.0	36.0	15.9
2	28	21.8	21.8	18.4
2	31	20.8	20.8	16.7
2	34	23.1	23.1	7.6
2	41	30.4	30.4	23.9

Characterisation of Marker/Coating System

A number of coated bottles with different marker concentrations (1.0 wt% and 0.1 wt%) were prepared for testing. As well as clear bottles of known geometry/surface area, a couple of post-consumer coloured bottles were coated to determine whether any effect of underlying colour on the fluorescence of the coating could be observed (*Figure 9*).

Figure 9. Photographs showing the bottles prepared for initial testing, from left to right: control, formulation 2 on clear, formulation 1 on clear, formulation 2 on light green, formulation 2 on dark green.

Firstly, the visible colour of the coated bottles was evaluated using spectrophometry and the CIELab system. The Petcore protocol for rPET quality control was used as the pass/fail criteria and results are shown in *Table 3*. Formulation 1, with 1.0% marker, clearly gave a visible change in colour as can be seen in *Figure 9*. This coating fails the PETcore test protocol on the basis of Δb* and ΔE, which shows a shift into the yellow. Formulation 2 passes the protocol. Therefore M2 must be used with maximum concentration in the region of 0.1 wt% to avoid colour changes to bottles.

Table 3. CIELab transmission results for spray-coated clear PET bottles with different levels of M2. L* indicates brightness, a* indicates the red/green balance of hue and b* indicates the blue/yellow balance of the hue. Δ indicates the change in such values relative to a control and ΔE is the calculated overall change.

Formulation ID	[Marker] (wt%)	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
PETcore protocol	N/A	>87	>-3				<1.5	<3
Control	N/A	95.74	-0.01	0.35				
1	1.0	93.78	-2.02	4.43	-1.96	-2.01	4.08	4.95
2	0.1	95.07	-0.12	1.35	-0.67	-0.11	1.00	1.21

Fluorescence from the bottles was next evaluated, visually, and using the bench-top detection system described in the experimental section. Photodiode detection and photography of the samples under UV irradiation are shown in *Figures 10 & 11* for clear bottles and green bottles

respectively. Exposure time of the detector was 500 μs and illumination was presented from both sides of the samples to minimise shadows. Figure 10 clearly shows the improvement in signal to noise that can be achieved by the inclusion of a long pass filter: background and spiking associated with the PET fluorescence and UV illumination scatter are both reduced significantly on addition of the filter. Even coating formulation M2, with only 0.1 wt% marker content can be detected in this manner and further optimisation may be possible. Detection of green-coloured bottles with this same formulation is more challenging. In *Figure 11* it can be observed that the coated dark green bottle gives a similar detector response to the uncoated clear control. A significant portion of the emitted light must pass through the bottle to reach the detector, therefore the lack of response was attributed to absorbance of the green fluorescence emission by the green dye in the bottle. The coated light green bottle was clearly distinguishable from the uncoated clear control, presumably due to the smaller quantity of dye present. An alternative explanation might be differences in coating grammage between the coloured bottles: this parameter was not measured for these samples so further work is clearly needed to understand and optimise the detection of coloured food contact bottles in this waste stream.
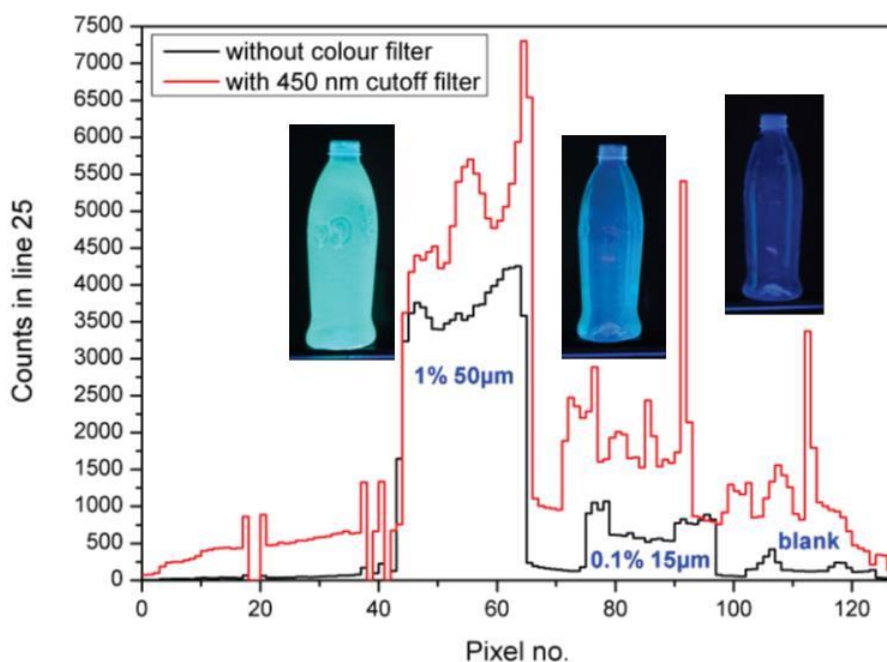

Figure 10. Comparison of photodiode response in the absence and presence of longpass filter (440 nm cutoff) showing response to clear bottles coated with formulation 1 (left), formulation 2 (centre) and blank (right).
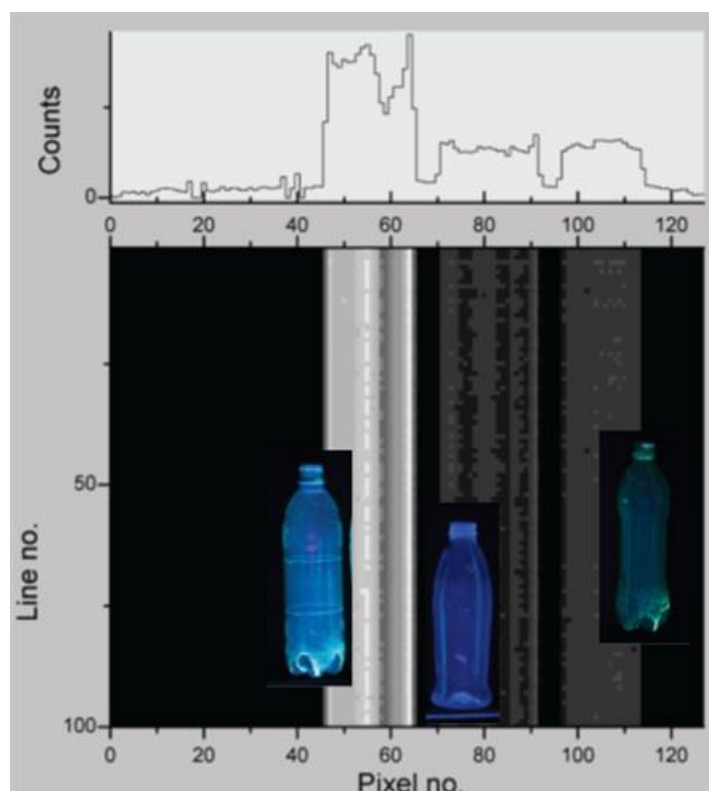
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Figure 11. Comparison of photodiode response from left to right: formulation 2 on light green bottle, blank, formulation 2 on dark green bottle.

Marker/Coating Removal Tests

Recycling plant flake washing was simulated using dip-coated extruded PET film cut into 5-10 mm pieces and sodium hydroxide solutions/temperatures typical for existing recycling processes as described in the experimental section. No significant difference in residual marker fluorescence was noted due to variations in wash conditions. *Figure 12* shows a representative example of the results. The coating was predominantly removed by the washing process, but the presence of small coated regions can still be observed. It was hypothesised that rinsing with hot water after washing was leading to re-coagulation of dispersed coating onto the flake, so a wash process using a rinse with sodium hydroxide solution was tested and found to give significant improvements over the single stage wash process. Traces of coating were still observed, but it is expected that washing would be more efficient on the larger scale due to higher flake content in the mixer and more vigorous agitation (leading to greater friction between flakes).
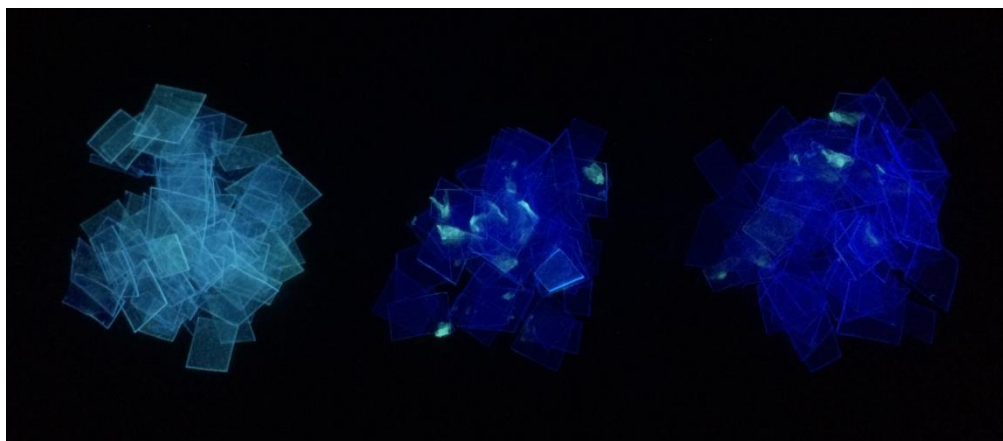
![Polymark logo]

Figure 12. Photograph under UV (365 nm) illumination from left to right: coated PET flake (1.0% marker), coated PET flake after washing in 2% sodium hydroxide at 60°C for 10 minutes followed by hot water rinse, coated PET flake after washing in 2% sodium hydroxide at 60°C for 10 minutes followed by caustic rinse.

In case of a situation where marker removal is incomplete, small concentrations of M2 were compounded into PET to evaluate its effect on PET fluorescence and mechanical properties: impurities in rPET are known to affect its degradation on re-extrusion and associated properties such as colour, tensile strength and molecular weight. Additionally, in a recycling system where PET returns repeatedly to the recycling plant and where food contact marked PET may end up in non-food contact applications, it is important to ensure that traces of residual marker do not contribute to future false positive detection of non-food contact material as food contact material.

A potential shift in the fluorescence spectrum between the compounded and coated markers was observed during these experiments and was investigated further using fluorescence spectroscopy. *Figure 13* shows the observed shift from green (λ_{max} = 505 nm) to blue fluorescence (λ_{max} = 440, 470 nm) that was observed and attributed to the change in state from an aggregated, particulate "pigment" (in the coating system) to a dissolved "dye" (in the compounded system). Such changes in fluorescence wavelength for benzoxazole fluorophores on changes in their chemical environment are well known (Mac et al., 2007). The fluorescence maximum for **M2** in polyester found in this investigation is similar to that reported in 1,1,1-trichloroethane (λ_{max} = 430 nm) in relation to the use of this optical brightener in polyesters (Jervis, 2003). Such a spectral shift is fortuitous for the application, since if traces of marker remain after washing, on re-extrusion their fluorescence will change and they will no longer be identified as food contact materials by the detection system.
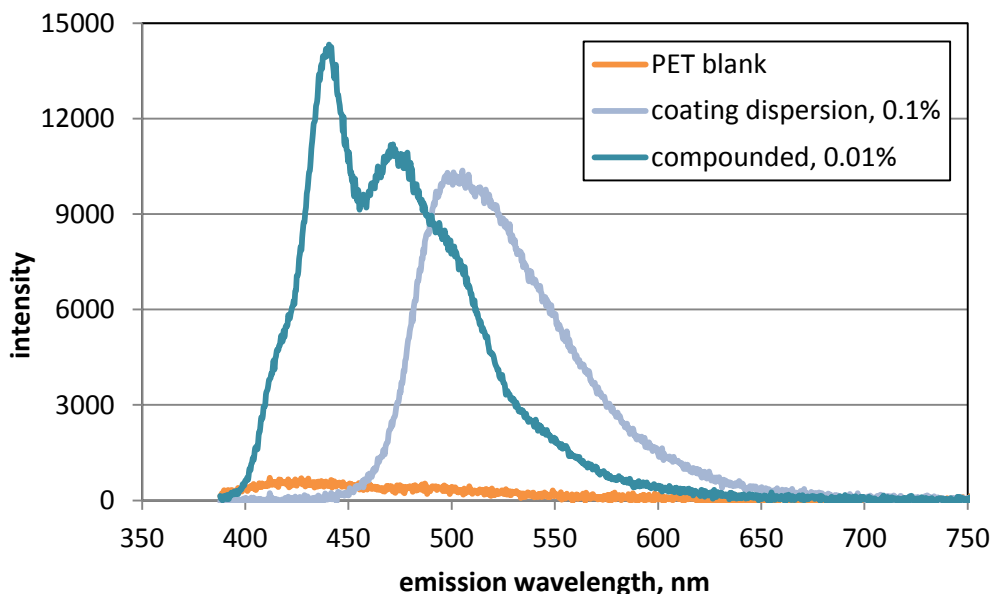
Figure 13. Comparison of fluorescence spectra of dispersed marker "pigment" and compounded marker as "dye".

Tensile properties were found to be unaffected by the presence of marker at levels of 0.01 and 0.1 wt%, indicating its inertness in PET. The maximum marker contamination that might be expected if coating removal is incomplete is estimated to be in the order of 5×10^{-5} wt% (or 0.5 ppm)[4], which is orders of magnitude lower than the levels tested. The effect of coating polymer residues on PET properties after re-extrusion has not, however, been evaluated. Acidic impurities (such as degradation products of PVC) in rPET waste streams tend to give rise to degradation and discolouration of PET due to chain scission processes even at low levels (Paci and La Mantia, 1999, 1998). Therefore, it could be conceivable that traces of acrylic acid groups from the coating polymer might have a similar effect. Also possible would be an acid-catalysed transesterification process between ester linkages of PET and acrylic acid leading to broadening of molecular weight distributions, as used in blend compatibilisation (Gravalos et al., 1995; Kim et al., 1997; Litmanovich et al., 2002). The authors are not aware of any study that has been performed to investigate the effect of low levels of poly(acrylic acid) contamination specifically on rPET properties, therefore it seems prudent to ensure that as much of the coating is removed in the washing process as possible.

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[4] Calculated using estimated residual coating as 1% of original quantity (visually estimated from photographs of residual marker fluorescence under UV irradiation), original coating grammage of 20 g m^{-2}, marker content of 0.1 wt% in coating, bottle mass of 34 g and bottle surface area of 0.6385 m^2.

Summary & Conclusions

A predominantly food contact approved, coating-based approach for the addition of a fluorescent marker to PET bottles has been developed with the following benefits:

- Use of commercially available, near UV-excitable markers with strong fluorescence in the visible region of the electromagnetic spectrum to allow development of a detection system with minimal UV/ozone generation hazards
  - The most suitable markers were found to be the food contact approved fluorescent brighteners 4,4'-bis(benzoxazol-2-yl)stilbene and 2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene
  - Stable dispersions of the preferred marker candidates above were achieved. The hyperdispersant was the only formulation ingredient lacking food contact approval.
  - In particular, the use of 4,4'-bis(benzoxazol-2-yl)stilbene as a dispersed pigment gave a unique fluorescence fingerprint that can be distinguished from the same chemical when used in a molecularly dissolved form (e.g. as an optical brightener in plastics) or from other background fluorescence
  - Low levels of marker were required for detection due to their strong fluorescence

- Water-based, sprayable coating formulation to minimise use of VOCs with associated flammability hazards
  - Good water resistance of coating following drying
  - Sufficient robustness of mechanical properties to retain the coating during the bottle life cycle

- The coating approach to marking plastic articles provides flexibility for:
  - Addition of further, dispersible marker pigments to the coating formulation in combination to allow development of a coding system in the future
  - Extension of the system to alternative polymer types, such as polypropylene (subject to adhesion, which may require surface treatment)

- Coating removability under alkaline wash conditions already in use within recycling plants
  - To allow previous food contact status of plastic to be erased in case it subsequently goes into a non-food contact application
  - Temperature and sodium hydroxide concentration minimised to reduce costs without impacting on removal efficiency

Next Steps

Following the interim review, the Polymark project is moving into the next phase of detection and sorting infrastructure development and testing. During this phase, the coating-based marker system will be subjected to real-world environments, further testing and sorting efficiency trials and optimisation using the prototype detection/sorting equipment currently under development. Additionally, an economic analysis and environmental impact study are planned. The results of these activities will be reported in due course.

Following project completion, further optimisation of the coating may be necessary, for example to improve sustainability of the developed solution by looking at alternative polymer matrices and

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reducing the coating thickness. Coating properties such as water resistance may benefit from improvement through further formulation development and testing activities.

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References

Al-Salem, S.M., Lettieri, P., Baeyens, J., 2009. Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Manag. 29, 2625–2643.

Awaja, F., Pavel, D., 2005. Recycling of PET. Eur. Polym. J. 41, 1453–1477.

Becker, A., Luttermann, K., Claussen, U., Orth, P., Heiliger, L., Sayed, A.E., 1994. Method for the identification of plastics. US 5329127.

Bezati, F., Froelich, D., Massardier, V., Maris, E., 2011a. Addition of X-ray fluorescent tracers into polymers, new technology for automatic sorting of plastics: proposal for selecting some relevant tracers. Resour. Conserv. Recycl. 55, 1214–1221.

Bezati, F., Massardier, V., Balcaen, J., Froelich, D., 2011b. A study on the dispersion, preparation, characterization and photo-degradation of polypropylene traced with rare earth oxides. Polym. Degrad. Stab. 96, 51–59.

Brunner, S., Fomin, P., Kargel, C., 2015. Automated sorting of polymer flakes: Fluorescence labeling and development of a measurement system prototype. Waste Manag. doi:10.1016/j.wasman.2014.12.006

Dvorak, R., Kosier, E., Fletcher, J., 2013. Improving food grade rPET quality for use in UK packaging: Final report.

EC, 2011. Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food.

EC, 2008. Regulation (EC) No 282/20008: Recycled plastic materials and articles intended to come into contact with foods and amending regulation (EC) No 2023/2006.

EC, 2006. Regulation (EC) No 2023/2006 on good manufacturing practice for materials and articles intended to come into contact with food.

EFSA, 2012a. Scientific Opinion on the safety evaluation of the following processes based on VACUREMA Prime (R) technology used to recycle post-consumer PET into food contact materials: "LuxPET", "Jayplas", "PolyQuest" and "CIER". EFSA J. 10, 2827.

EFSA, 2012b. Scientific Opinion on the safety evaluation of the following processes based on Starlinger IV+ (R) technology used to recycle post-consumer PET into food contact materials: "Preformia, STF, PET to PET and Eco Plastic". EFSA J. 10, 2828.

Gravalos, K.G., Kallitsis, J.K., Kalfoglou, N.K., 1995. In situ compatibilization of poly(ethylene terephthalate)/poly(ethylene-co-ethyl acrylate) blends. Polymer (Guildf). 36, 1393–1399.

Hachin, J.-M., Lambert, C., 2009. Method for authentication by chemical marking or tracing of an object or substance. US 7605372 B2.

Hopewell, J., Dvorak, R., Kosier, E., 2009. Plastics recycling: challenges and opportunities. Philos. Trans. R. Soc. B 364, 2115–2126.

Jervis, D.A., 2003. Optical brighteners: Improving the colour of plastics. Plast. Addit. Compd. 5, 42–46. doi:10.1016/S1464-391X(03)00049-7

Kim, S., Park, C.E., An, J.H., Lee, D., Kim, J., 1997. The effect of functional group content on poly(ethylene terephthalate)/high density polyethylene blends compatibilized with poly(ethylene-co-acrylic acid). Polym. J. 29, 274–278.

Kosier, E., Davies, K., Kay, M., Mitchell, J., Ahmad, R., Billet, E., Silver, J., 2014. Optimising the use of machine readable inks for food packaging sorting: Final report.

Lambert, C., Hachin, J.-M., 2012. Method for recycling materials coming from used objects. US 8205813 B2.

Langhals, H., Zgela, D., Schücker, T., 2014. High performance recycling of polymers by means of their fluorescence lifetimes. Green Sustain. Chem. 4, 144–150.

Lee, K., 2013. Tags for the sorting of plastics. US 8574384 B1.

Litmanovich, A.D., Platé, N.A., Kudryavtsev, Y. V., 2002. Reactions in polymer blends: interchain effects and theoretical problems. Prog. Polym. Sci. 27, 915–970.

Luijsterburg, B., Goossens, H., 2014. Assessment of plastic packaging waste: Material origin, methods, properties. Resour. Conserv. Recycl. 85, 88–97.

Luttermann, K., Claussen, U., Sayed, A.E., Riess, R., 1993. Process for identifying plastics by addition of fluorescent dye. US 5201921.

Mac, M., Tokarczyk, B., Uchacz, T., Danel, A., 2007. Charge transfer fluorescence of benzoxazol derivatives - Investigation of solvent effect on fluorescence of these dyes. J. Photochem. Photobiol. A Chem. 191, 32–41.

Manikowski, H., Lijevvski, M., 2010. Fluorescence of poly(ethylene terephthalate) (PET) polymer induced by thermal and visible radiation, in: 3rd International Conference - Radiation Interaction with Material and Its Use in Technologies 2010, Program and Materials, Interaction'2010. Poznan University of Technology, Faculty of Technical Physics, Nieszawska 13A, 60-965 Poznan, Poland, pp. 64–67.

Maris, E., Aoussat, A., Naffrechoux, E., Froelich, D., 2012. Polymer tracer detection systems with UV fluorescence spectrometry to improve product recyclability. Miner. Eng. 29, 77–88.

McGuinness, W.G., Clay, B.J., 1984. Object recognition and identification system using ultraviolet fluorescent materials. WO 1984003646 A1.

Paci, M., La Mantia, F.P., 1999. Influence of small amounts of PVC on the recycling of PET. Polym. Degrad. Stab. 63, 11–14.

Paci, M., La Mantia, F.P., 1998. Competition between degradation and chain extension during processing of reclaimed PET. Polym. Degrad. Stab. 61, 417–420.

Packham, I., 2014. Special Report: R-PET uptake is taking off [WWW Document]. ICIS Chem. Bus. URL http://www.icis.com/resources/news/2014/03/07/9760473/special-report-r-pet-uptake-is-taking-off/ (accessed 5.28.15).

Petcore Europe, 2014. unpublished PET recycling data.

PlasticsEurope, 2015. Plastics - the Facts 2014/2015: An analysis of European plastics production, demand and waste data.

Puype, F., Samsonek, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M., 2015. Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold on the European market. Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk Assess. 32, 410–426. doi:10.1080/19440049.2015.1009499

Shen, L., Worrell, E., Patel, M.K., 2010. Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling. Resour. Conserv. Recycl. 55, 34–52.

Tachwali, Y., Al-Assaf, Y., Al-Ali, A.R., 2007. Automatic multistage classification system for plastic bottles recycling. Resour. Conserv. Recycl. 52, 266–285.

Welle, F., 2013. Is PET bottle-to-bottle recycling safe? Evalation of post-consumer recycling processes according to the EFSA guidelines. Resour. Conserv. Recycl. 73, 41–45.

Welle, F., 2011. Twenty years of PET bottle to bottle recycling - An overview. Resour. Conserv. Recycl. 55, 865–875.

World Economic Forum, 2014. Towards the Circular Economy: Accelerating the scale-up across global supply chains.