Final Report

Masking strength of NIR detectable black colourants

A summary report describing the masking capabilities of NIR detectable black colourants in rigid plastic packaging.

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Front cover photography: [PP packaging samples showing varying levels of masking strength performance of NIR detectable black colourants]

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Executive summary

Black plastic packaging is normally coloured with carbon black pigment which is low in cost, has high tint strength, can be used in food contact packaging, and provides a contrasting background which allows the colours in the food to stand out.

However, plastic packaging items produced with carbon black currently cannot be detected with automated Near Infrared (NIR) sorting systems used in the recycling of plastics and consequently almost all post-consumer black plastic packaging ends up in landfill. The use of NIR detectable black colourants in packaging would enable the plastic to be recycled to produce high quality materials (as can be achieved with non-black packaging) that can be used in place of virgin plastic to make new items. This would divert black plastic packaging from landfill and deliver savings in CO_2.

In previous work[1] a preliminary assessment of the masking potential and incremental costs of the novel black colourants in comparison to that of carbon black was carried out. It was clear from that preliminary test that the NIR detectable black colourants had relatively poor masking properties.

The ability to mask mixed colours is helpful to plastics processors as it allows them to re-use production waste and off-cuts of all colours. It also enables reprocessors to recycle a "jazz" stream (mixed colour) from MRFs and PRFs by blending them together and recycling them into black materials.

The aim was to investigate the masking strength of the detectable black colourants in comparison to carbon black pigment in more detail and to understand the implications of any inferior masking capabilities of the alternative black colourants for packaging convertors.

The masking strength trials have shown that the tested NIR detectable black colourants generally have poor masking properties when compared to carbon black at typically used addition rates of 1-2%. Detectable black colourants can effectively mask a variety of colours but the masking is only achieved at higher addition rates of 3-5%.

Multi-layer structures using the same polymer in all layers have the potential to provide an economically viable method for masking a variety of colours. This is because there is the potential to use cheaper carbon black in the inner layer, which has good colour masking properties and also enable the pack to be sorted by using detectable colourants in the outer layers. Using the same polymer in all layers means that recyclability is not adversely impacted and the use of detectable colourants in outer layers means that the packaging could be recovered for reprocessing. Tests performed on PP multi-layer structures showed that the sheet could be identified by the top 'cap' layer PP polymer, even when the middle PP layer was coloured with carbon black. This technique could be exploited to reduce the cost of using these colourants where multi-layer products are made.

While masking strength is important for some reprocessors of mixed coloured recycled flakes, for most converters, masking strength is less of an issue as coloured skeletal waste is stored separately and generally not mixed together. This is because once colours are mixed the value is typically reduced and for this reason the skeletal waste off cuts and trims are used up as regrind directly during production or future runs.

This approach preserves the value of the coloured polymers and by storing the coloured skeletal off-cuts and trims separately; it allows the converters to maintain the value of these materials for future production runs. A key finding from investigations in this project was that UK converters generally do not mix coloured skeletal waste and therefore inferior

[1] *Development of NIR Detectable Black Plastic Packaging* http://www.wrap.org.uk/content/recyclability-black-plastic-packaging-0

masking strength is not a limiting factor for most converters in the UK and the detectable colourants may be suitable to use without the need for high masking strength.

The cost of the detectable colourants is likely to decrease as demand increases and further research and development improves the economics and properties of detectable black colourants. It is anticipated that there will be growing interest in evaluating and implementing NIR detectable black colourants by retailers and converters so that the black plastic packaging they produce can be recycled at all automated recycling facilities.

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Glossary of Terms

ABA	An ABA multi-layer structure refers to the encapsulation of material B in the middle layer by material A in the outer 'cap' layers
APET	Amorphous form of Polyethylene terephthalate
Colourant	Use to describe either a dye or a pigment
CPET	Crystallised form of Polyethylene terephthalate
DBP	Detectable black plastics (black plastics that can be identified by near infra-red spectroscopy and polymer type can be determined)
Dye	Organic often soluble compound dispersed in the polymer to provide a colour
EFSA	European Food Safety Authority
Food Contact Polymer or Packaging	That which has been used in contact with food or has been tested and approved for use in contact with foods in compliance with the requirements of EU Regulation 10/2011.
HDPE	High-density polyethylene.
IR	Infrared
MFR or MFI	Melt Flow Rate or Melt Flow Index; a rheological test method providing an assessment of ease of flow within subsequent melt processing equipment. Also an indicator of molecular weight.
MRF	Material Recovery Facility

NIR	Near infra-red
PCR	Post-consumer recyclate
PET	Polyethylene terephthalate
Pigment	Fine organic or inorganic solid compound dispersed in the polymer to provide a colour
PP	Polypropylene
ppm	Parts per million
ppb	Parts per billion
PRF	Plastic Recovery Facility
Residence time -	Time spent under specific processing or decontaminating conditions
rHDPE	Recycled high density polyethylene
rPET	Recycled polyethylene terephthalate
rPP	Recycled polypropylene
TiO_2	Titanium dioxide, TiO_2 is a commonly used white pigment in the plastics industry

Acknowledgements

Nextek Limited would like to thank the project partners for valuable technical support, expertise and helping Nextek ensure that the project trials were completed efficiently and on time.

We would specifically like to thank the following organisations:

Colourtone Masterbatches for the time spent by its staff in optimising the masking strength of its range of NIR detectable colourants for PP and APET/CPET, the provision of masterbatches for several injection moulding and sheet extrusion trials in the UK and Denmark.

ColorMatrix for the on-going technical advice and all the support given by ColorMatrix staff and the time spent on masking trials, production of preforms and development and provision of a solid form of the Dye Black-5 colourant for trials on PET products.

Holland Colours for investigating potential methods to improve the masking strength of its detectable black colourants.

FærchPlast for the support they have provided to this project by running a series of multi-layer CPET sheet extrusion trials.

Sharpak for providing samples of regrind and for performing PP sheet extrusion trials to test the masking strength of the NIR detectable black colourants and for providing tray samples for visual assessments.

RPC for providing samples of regrind and for performing a series of injection moulding trials to test the masking strength performance of detectable black colourants in PP tubs.

LINPAC for providing samples of mixed colour regrind and feedback on reprocessing of mixed colours.

TITECH GmbH for the many NIR tests that TITECH staff performed to evaluate detectability of all the samples from these trials and the valuable feedback and technical advice on the results obtained.

Finally, we would like to thank Peter Crome and Mark Christopher for photographing the packaging samples produced as part of this project.

1.0 Introduction and overview of the project

Introduction

Black plastic packaging is normally coloured with carbon black pigment which is low in cost, has high tint strength, can be used in food contact packaging, and provides a contrasting background which allows the colours in the food to stand out.

However, plastic packaging items produced with carbon black currently cannot be detected with automated Near Infrared (NIR) sorting systems used in plastics recycling and consequently almost all post-consumer black plastic packaging ends up in landfill.

This project builds on the previous project 'Development of NIR Detectable Black Plastic Packaging' http://www.wrap.org.uk/content/recyclability-black-plastic-packaging-0

That project demonstrated the potential for black plastic packaging to be sorted by polymer type and recycled. Novel NIR detectable black colourants were developed and shown to look satisfactory in APET, CPET and PP food trays, and enable the packaging to be sorted by polymer type using NIR sorting systems used commercially in plastics recycling facilities. The use of NIR detectable black colourants in packaging would enable the plastic to be recycled to produce high quality materials (as can be achieved with non-black packaging) that can be used in place of virgin plastic to make new items. This would divert black packaging from landfill and deliver savings in CO_2 emissions.

Background

The ability to mask mixed colours is helpful to plastics processors as it allows them to re-use production waste and off-cuts of all colours. It also enables reprocessors to recycle a "jazz" stream (mixed colour) from MRFs and PRFs by blending them together and recycling them as black coloured materials. Carbon black is generally used to mask mixed colours, however this results in the production of a black resin, and subsequently packaging, that would not be detectable and could not be widely recycled.

In the WRAP project 'Development of NIR Detectable Black Plastic Packaging' Nextek investigated the masking potential of the novel colourants and compared them with carbon black. It was clear from those preliminary tests (involving the masking of a white pigment to represent a severe case) that the NIR detectable black colourants had poorer masking properties compared to carbon black. Consequently it was thought that the colours that could be included in a 'jazz' fraction to be subsequently coloured black using the alternative black colourants may be limited to a dark colour stream such as greens, blues and browns.

Project objectives

The objective of this project was to provide a more complete understanding of the masking capabilities of the NIR detectable black colourants. The investigations involved a series of masking trials to assess the ability of the colourants to mask a range of colours, strengths and addition rates that a packaging convertor would expect to get in their manufacturing processes. This would then provide more detailed information to convertors about the performance of NIR detectable colourants in a range of situations.

A key component of the research work was to establish whether the colourants could be used as they are, and conceal a range of colours or identify whether further optimisation work is needed. This report also investigates strategies to cope with any masking deficiency found, and stock control measures that could be implemented by convertors to optimise usage of coloured regrind materials within their operations. This report also investigates methods that could be used to maximise the masking effect of the NIR detectable colourants.

Project methodology

This project explored masking properties using a designed experiment conducted by the colourant suppliers, Colour Tone Masterbatch Ltd and ColorMatrix Group.

The first steps included acquisition of a variety of coloured PP, APET and CPET samples from in-house convertor trims and off-cuts. Project participants Sharpak, RPC, LINPAC and Færch Plast were all asked to supply two samples of regrind materials that they would typically colour black. One sample was to be a light colour mix that would be challenging for the NIR detectable black to mask and one samples was to be a dark mix that would be less challenging. Both samples had to exclude any existing black materials and carbon black to ensure that the resultant material would still be NIR detectable.

The next steps involved conducting blending and injection trials to make a range of test plaques and preforms in PP, CPET, APET using different blends and colour mixes of in-house convertor skeletal trim/off-cuts coloured with NIR detectable colourants. NIR detectable colourants identified in the previous project work were blended at selected addition rates with different quantities of collected regrind materials as well as virgin materials, and then injection moulded into plaques and preforms. The plaques and preforms were then assessed for colour masking performance and level of black opacity achieved.

The results shown by the plaques and preforms from the initial masking strength trials on regrind supplied by packaging converters were ranked and the best performing sample blends that appeared to provide acceptable masking performance were selected after discussions with the colourant suppliers. The assessment also included discussions on the range of trim/off-cut colours that could be successfully masked by the colourants in PP, CPET and APET and which colours would be difficult to mask based on preliminary results. The results obtained in the plaque and preform test trials were also shared and discussed with converters prior to colourant optimisations and large-scale trials.

The colourant suppliers were then asked to make any possible adjustments to the masking performance of the colourant and advise optimum addition rates for large-scale sheet extrusion and injection mould trials using PP, CPET and APET.

Plaque and preform samples were sent for NIR polymer detection trials at TITECH in Germany. Assessments of NIR detectability of the PP, CPET and APET plaques and preforms were made and the recognition level (ease) of detection was measured and recorded.

The potential of using multilayer structures to mask mixed colours with detectable black colourants was assessed in sheet extrusion trials and the NIR detectability of multilayer structures was tested.

Large-scale injection moulding and sheet extrusion trials were performed by RPC, Sharpak and Færch Plast and included the production of pots and single layer and multi-layer trays. Products produced during large scale trials were sent to TiTech for NIR polymer identification testing to ensure that the products were NIR detectable.

2.0 Assessment of detectable black colourant's masking strength on a variety of colours

RPC, LINPAC, Sharpak and Færch Plast were contacted for samples of mixed light coloured and dark coloured regrind materials that they may typically re-colour internally with carbon black.

Sharpak advised that it does not generally have much in-house scrap or trim regrind, it re-uses any skeletal trim, off-cuts and production scrap almost immediately whilst the product is being produced. For this reason Sharpak was unable to initially supply any mixed colour regrind material for this project.

Færch Plast doesn't mix coloured regrind but always keep each colour separate because the materials may have different impact strengths which could affect its final products. Therefore the colours are not mixed and masking strength is not considered to be an issue for Færch Plast. For the preliminary masking trials Færch Plast agreed to supply ivory and terracotta coloured CPET flakes.

Figure 1. Example of the terracotta and ivory CPET regrind supplied by Færch Plast.

RPC was asked for standard production regrind samples and it also indicated that it does not mix its regrind colours but keeps them separate to maintain the coloured resin value. RPC did not have any dark colours available to send and therefore it supplied natural and cream coloured PP flakes.

Figure 2. Natural and cream PP regrind supplied by RPC.

LINPAC advised that in general it uses its in-house scrap day by day, hour-by-hour so could only supply samples of the colours it was running on the day. This means that LINPAC does not typically mix colours and like Sharpak try to use-up any off-cuts and trims for current production. LINPAC supplied silver APET flakes, which contain 50% recycled PET and also have an LDPE sealing layer.

Figure 3. Silver APET regrind supplied by LINPAC.

The feedback from convertors suggests that very few actually mix colours. This is because once colours are mixed the economic value is typically reduced and for this reason the off cuts and trims are used up directly during production.

All the manufacturers were also asked to provide samples of current products made with carbon black. These samples were used as controls during the masking strength assessments.

Figure 4. Black control samples supplied by Færch Plast, RPC and LINPAC

2.1 Masking Strength Testing

Each of the coloured regrind trim samples were sent to ColourTone, ColorMatrix and Holland Colours for masking strength optimisation and all colourant suppliers were asked to provide plaques coloured with carbon black to give a direct comparison of the relative covering merits of each.

To improve the covering power of the current NIR detectable liquid colourants and masterbatches, the colourant manufacturers evaluated a number of possibilities.

These included:

- Increasing the colourant levels, as the NIR detectable colourants were previously formulated with minimal colourant due to the high cost of some components. The optimised colourants would have higher tint strength and therefore provide the more effective masking solution for light-coloured and natural polymers.
- Including other NIR colourants into the current black formulation that might have better covering power in the black masterbatch than the existing formulation.

Given that many pigments (not only carbon black) are infra-red (IR) absorbing, the colourant suppliers were asked to pay particular attention to ensuring that the NIR detectability would not be compromised. Some colours, even pastel colours such as ivory, may include carbon black as a tinting agent, which could have an effect on the IR transparency. To avoid this distortion, trials were performed using TiO_2 (Titanium dioxide, a white pigment) to evaluate the relative covering power of the black colourants in natural polymer with a known TiO_2 level so removing a potential distortion of the result or another source of failure.

2.1.1 Plaque manufacture

In order to asses a series of blends in a designed experiment, the colourant suppliers manufactured test pieces using current NIR detectable colourants identified in the previous project work and blended these with different quantities of the collected materials and virgin materials, by injection moulding the blends into plaques, a common process for colour matching in the colour industry.

These industry standard plaques have steps of reducing thickness from which qualitative and quantitative measures of colour and opacity can be made. This method offers a fast, simple and low cost method to benchmark masking properties of the NIR detectable black colourants when mixed with different colour of regrind.

The ranking of results provided a basis for the selection of blends that provide acceptable masking performance. Using this same technique samples could be developed to rapidly test new and improved NIR detectable black colourants, the best performing of which could be then be selected for further evaluation.

2.1.2 Preliminary Colour Tone optimisation trials for PP & CPET and APET

Colour Tone Masterbatch Ltd performed a series of masking trials and reported that they were able to slightly increase the opacity and improve the black finish without compromising the IR properties, and also further optimised the colourant for PP to maintain the original black colour.

Colour Tone suggested testing its optimised masterbatch on samples of 10% and 25% regrind in prime polymer (as this is the usual industrial practice) and also produced samples with a carbon black masterbatch. Both the carbon black and the optimised detectable black colourant for PP were then tested for their masking strength with a known level of TiO_2 compound to get a quantitative assessment of the effectiveness of each. Colour Tone produced test compounds and then moulded 116 sample plaques in the different materials, at 0.5%, 1.0%, 2.0% and 5.0% addition rates to test the colourant performance.

Colour Tone performed a series of further developments for a detectable masterbatch for CPET and APET. For the PET masterbatches they performed tests to ensure that there were no leaching issues at PET processing conditions and also when tested using hot oil.

2.1.3 Preliminary ColorMatrix optimisation trials for PET

ColorMatrix received APET and CPET regrind samples and focused on optimising an improved version of Dye Black-5 colourant for APET and CPET applications. ColorMatrix performed several trials using 100% coloured regrind and found that the Dye Black-5 colourant proved suitable for covering up other PET colours and in general showed good coverage at 2% addition rate.

The trials at ColorMatrix were performed on a preform injection moulding line, as the laboratory injection moulder for plaques was not designed for regrind flakes (designed for pellets only with a small in-feed).

a) 100% Cream CPET regrind with (l-r) 0.5, 1.0, 2.0 and 5.0% Dye Black-5

b) 100% Silver APET regrind with (l-r) 0.5, 1.0, 2.0 and 5.0% Dye Black-5

c) 100% Terracotta CPET regrind with (l-r) 0.5, 1.0, 2.0 and 5.0% Dye Black-5

Figure 5. Preliminary masking strength results using Dye Black-5 with a variety of light and dark PET colours.

2.1.4 Preliminary Holland Colours optimisation trials in PET and PP

Holland Colours was sent regrind samples for development trials using its Holcobatch NIR detectable black colourant, which proved to be NIR detectable in previous trials. This development was still under way at the time of these investigations and due to time constraints, samples from Holland Colours were not included in the large-scale trials.

3.0 Optimisation and R&D into improved detectable black plastics

3.1 Colour Tone optimisation trials

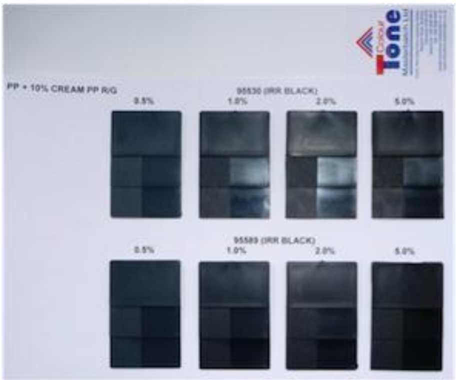
After initial laboratory assessments of the IRR 95530 pigment masking strength performance in PP, Colour Tone reported that it was able to increase the opacity/masking power of the IRR masterbatch to a small extent by changing the formulation and slightly increasing the total pigment level; any further development would need to be done on a full-scale production run of the IRR masterbatch to determine whether it is possible to increase further the pigment level and still be able to manufacture the masterbatch successfully.

The reference for the original PP masterbatch is 95530 and that for the improved formula is 95589.

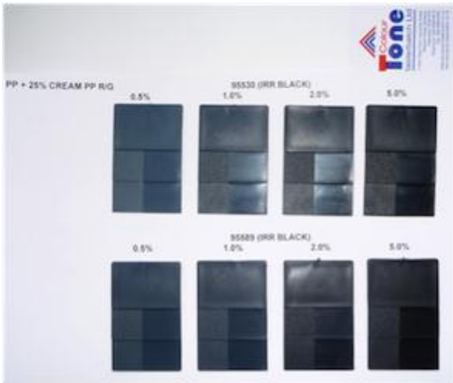
To give a controlled comparison between the original formulation and the revised version, a set of samples were made using regrind as well as a standard level (1%) of titanium dioxide in virgin PP. This was done to illustrate more accurately the difference between the two masterbatches and the progressive change in colour when increasing the addition level of the IRR black than is shown by the samples containing regrind, which can be prone to some variation due to the flaky nature of the regrind material.

Also included was a standard carbon black masterbatch at 1% for comparison to the IRR masterbatches.

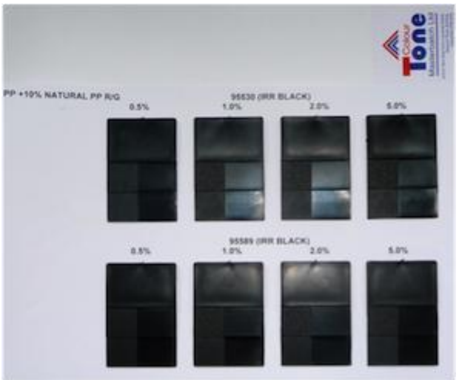
The plaque samples shown in Figure 6 were moulded using blends of the different regrind samples with virgin resin and a range of addition rate of the IRR blacks. The bottom row of each picture uses the optimised version of the detectable colourant (95589).



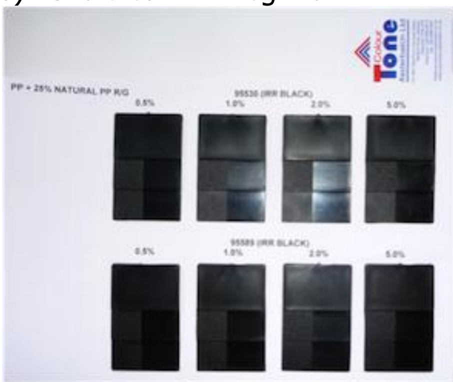
a) 10% cream PP regrind



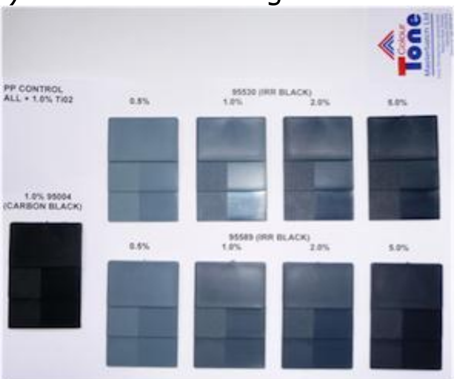
b) 25% cream PP regrind



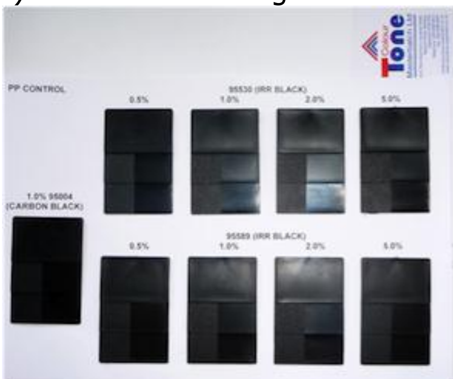
c) 10% natural PP regrind



d) 25% natural PP regrind



e) virgin PP + 1% TiO_2 with 1% CB on the left



f) virgin PP only + 1% CB sample on the left

Figure 6. 10% and 25% regrind with virgin Polypropylene plaques using Colour Tone IRR 95530 (top row) and IRR 95589 (bottom row) with addition rates of (l-r) of 0.5%, 1.0%, 2.0% and 5.0%.

The range of shades achieved using the IRR blacks with the cream-coloured regrind supplied by RPC (6a and 6b) illustrates the masking properties achievable with a challenging environment.

Figures 6a and 6b show the cream PP regrind blended with virgin PP at 10% and 25% and then coloured with the two IRR black samples in a range of addition rates from 0.5 – 5.0%. In industrial production plants it is highly unlikely that such a pale coloured regrind would normally be used in a black product based on the comments of the convertors mentioned earlier. However at the 10% addition rate of the cream coloured regrind, a dose level of 2% of both black colourants appear to provide sufficient coverage. Discussions with Sharpak and Colour Tone suggested that 2% colourant addition rate should be used in the large-scale trials on commercial production equipment. When trialled on 25% cream regrind content a successful coverage is achieved close to 5% addition rate, however a lower addition rate may be possible and refinements may need to be performed as 3-4% may also prove to be sufficient.

In figure 6c and 6d the regrind used was natural (colourless) so it was expected that the IRR colourants would successfully cover at the lower levels of 0.5% addition rate. As expected, the natural regrind samples did not show any difference in appearance from the control samples shown in 6f.

Figure 6e compares the samples based on natural PP and 1% TiO_2 compounded with a range of masterbatch levels of the two colourants. When compared with the 1% carbon black sample on the left in Figure 6e, the samples show that up to 5% addition of the detectable colourants is needed to match the coverage of only 1% carbon black when added to 1% titanium dioxide (TiO_2). The carbon black plaque clearly shows that even at 1% it has superior masking strength. Lower addition rates of 3 or 4% of the optimised detectable black were not tested to see if these levels were adequate in these trials due to time constraints.

Colour Tone also developed PET masterbatches suitable for both CPET and APET applications. The PET IRR 95559 was the original formula and IRR 95591 was the optimised version for PET trials. Both 95559 and 95591 at 2% were used in large-scale trials.

3.1.1 ColorMatrix optimisation trials

ColorMatrix reported having some issues with processing associated with feeding the flakes into the laboratory plaque moulding machine due to the large size of regrind flakes from skeletal waste. For this reason only a few of the CPET and APET materials were moulded in plaque form before they switched to a larger preform moulding machine, where a wider throat and barrel helped with the feeding issues.

For the PP regrind it was not possible to use the dye based colourant (which is suited to amorphous plastics like APET and not suited to polymers like PP due to a lack of miscibility with crystalline polymers) and ColorMatrix has continued researching pigment based products that are still under development. The samples shown in Figure 7 are CPET regrind samples of the cream / ivory CPET regrind supplied by Færch Plast all run at 100% and coloured with increasing percentages of ColorMatrix Dye Black-5 (DB-5).

Figure 7. 100% Cream/ivory CPET regrind mixed with ColorMatrix Dye Black-5 at (l-r) 1%, 2% and 5% addition rate. The carbon black tray in the background is used for comparison.

ColorMatrix evaluated the dye based colourants by moulding performs as this is its standard method of conducting colour comparisons. The thicker walls of the preforms would not influence the colour comparison results since all of the components would be opaque even at thin wall thickness. As with the cream coloured PP regrind, it is unlikely that such a pale coloured regrind would typically be used in a black CPET product (making this a challenging test) however an addition level of above 2% and below 5% was considered to give sufficient coverage of these 100% regrind samples based on the evaluations of ColorMatrix.

Figure 8 shows the 100% silver APET regrind supplied by LINPAC coloured with 1.0, 2.0 and 5.0% Dye Black-5. From these samples an addition rate above 1.0 and up to 2.0% was found to give an acceptable black colour. However there was some concern that the metallic particles from the silver were still visible in the moulded preforms when held against the light.

Figure 8. 100% Silver APET regrind mixed with 1.0, 2.0 and 5.0% Dye Black-5. A carbon black tray in the background is for comparison.

Figure 9: 100% Terracotta CPET regrind mixed with 1.0, 2.0 and 5.0% Dye Black-5. A carbon black tray in the background is for comparison.

In figure 9 the terracotta CPET regrind supplied by Færch Plast was also coloured with 1.0, 2.0 and 5.0% Dye Black-5. From these samples it was determined that an addition rate of between 1.0 and 2.0% gives an acceptable black.

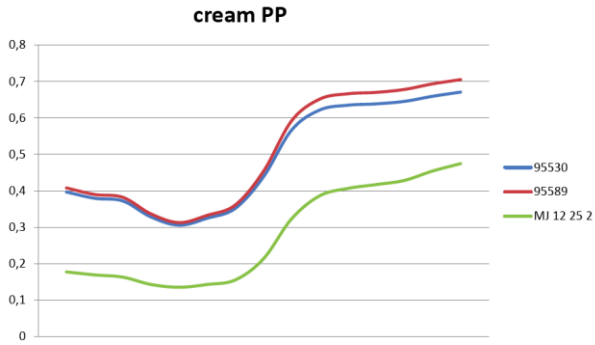
Figure 10: Comparison of masking strength on a variety of 100% regrind colours at 2 and 5% addition rates.

In summary, the masking of the 100% silver and 100% opaque cream/ivory materials can be considered to be challenging for Dye Black 5 colourant. The trials showed that the Dye Black-5 had good masking properties and was able to provide complete coverage between 1-2% addition rate for tinted colours and even less for dark opaque colours. For opaque solid cream/ivory colours at 100% usage, a much higher addition rate (5%) would be required and masking at lower addition rates was poor.

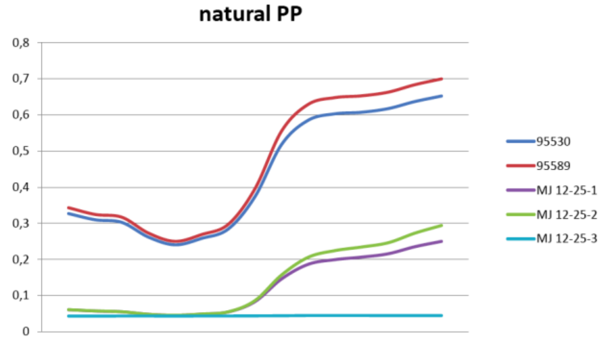
3.2 NIR detectability tests on plaques and preforms

NIR detection tests on 32 of the most promising samples were performed at TITECH in Germany. The samples included plaques and preforms moulded with a variety of detectable black colourants at addition rates ranging from 0.5%-5.0%. Two control samples, commercially made APET and CPET trays containing carbon black were also tested.

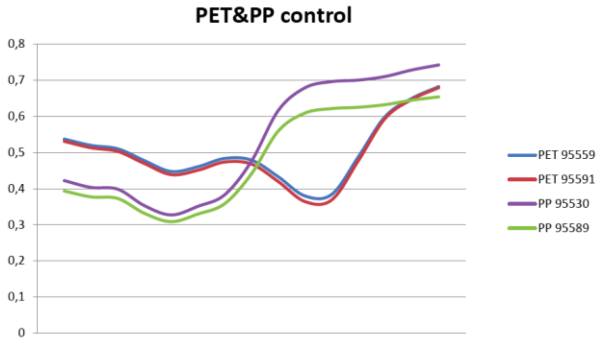
The results indicated that all the colourants developed including the optimised grades, were detectable using NIR polymer identification technology. The polymer type of some samples was easily recognised while other samples were more difficult to detect and further sensor training and software adjustment by the sensor manufacturers would be needed to ensure comprehensive identification.



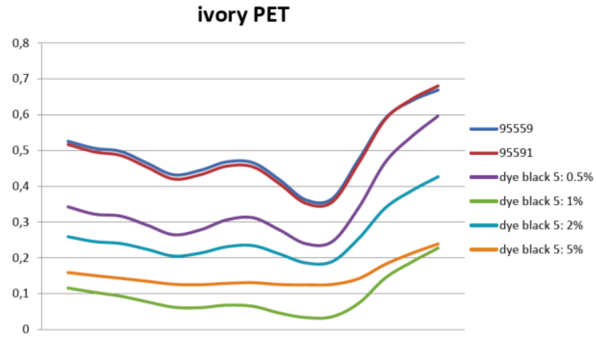
a) NIR detection signal strength in cream coloured PP masked with detectable black colourants (top two plots) and the control 25% cream colour sample (MI 12252).



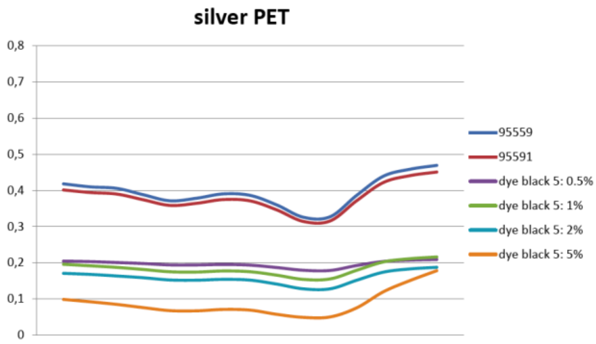
b) NIR detection signal strength in natural PP masked with detectable black colourants (top two plots, 10 and 25 % cream control samples (mid two plots) and a carbon black control (MI 12253).



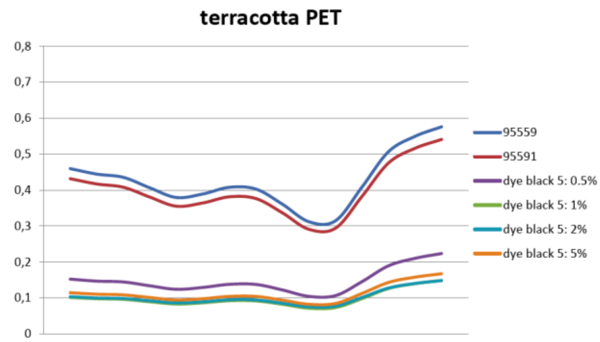
c) NIR detection signal strength in PP and PET samples masked with detectable black colourants.



d) NIR detection signal strength in ivory coloured CPET masked with detectable black colourants.



e) NIR detection signal strength in silver coloured APET masked with detectable black colourants.



f) NIR detection signal strength in terracotta coloured CPET masked with detectable black colourants.

Figure 11: Example of NIR plaque and preform detection results in PP, CPET and APET samples that have been coloured with a range of developed detectable black colourants.

The results of the trials showed that the samples using the Colour Tone colourants were easier to identify, however these samples had 10% or 25% coloured regrind while the preform samples with ColorMatrix colourants were made with 100% coloured regrind. The ColorMatrix Dye Black-5 coloured PET sample was readily identifiable when mixed with terracotta and ivory coloured PET regrind even at 100%, but was more difficult to identify in the 100% silver blend. Samples of Dye Black-5 appeared to be visually darker and have stronger masking characteristics than the Colour Tone pigmented materials, however with

100% levels of coloured regrind some of the signals were too low to allow polymer detection.

4.0 Research into masking performance using multi-layer sheet extrusion techniques

Multi-layer structures using the same polymer in all layers have the potential to provide an economically viable method for masking a variety of colours. This is because cheaper carbon black pigment which has good colour masking properties could be used in the inner layer with mixed colour regrind flakes, but the use of detectable colourants in the outer layers would enable the pack to be optically sorted by recyclers.

A trial to determine the potential of multi-layer structures at masking mixed colours was performed at Queen Mary University. The advantage of doing this would be to use potentially higher levels of the detectable masterbatch in thinner outer layers to obtain opacity. This might allow a range of mixed colours to be used in the internal layer as well as potentially any carbon black pigmented materials. This may allow savings in material costs as well as providing good colour and surface finish.

Several runs were used to manufacture of a 3-layer sheet and mono layer sheet. The products produced were:

1. A 3-layer structure which contained a 500 micron (µm) middle layer of white PP and a 70 micron (µm) LDPE cap layer coloured with a detectable black colourant, Colour Tone IRR 95589. This trial was performed to determine the masking ability of an outer layer coloured with a detectable black colourant. Two samples were sent for testing.
2. A 3-layer structure which contained a 500 micron middle layer of PP coloured with carbon black and a 70 micron LDPE cap layer coloured with a detectable black colourant, Colour Tone IRR 95589. This trial was performed to determine whether it is possible to detect a polymer by the thin outer layer when the middle layer contains carbon black.
3. Mono layer of 300 micron thickness of PP of only white regrind and then white regrind with 1% carbon black.

In normal practice the outer layer would be the same polymer as the core layer, in this case PP, however LDPE resin was used for the outer 'cap' layer instead of PP so that it would be possible to separate the top LDPE and middle PP layers to allow simple delamination and thickness measurement.

a) example of the white PP middle layer in the process of being coated with a detectable black layer.

b) the use of a detectable black colourant in a top layer demonstrates masking ability.

Figure 12. Example of multi-layer PP sheet being extruded into an ABA structure with white regrind in the middle layer and detectable black colourant in the outer layers.

The trials confirmed that a multi-layer structure could be an efficient and a cost effective method for masking mixed and light colours in a middle layer. Samples of the mono and multi-layer LDPE/PP/LDPE sheets including those containing carbon black in the PP middle layer were sent to TITECH for NIR detection testing. The test results are discussed in section 6.0.

5.0 Large-scale masking strength assessment trials

In order to test the masking strength performance on commercial packaging products a series of large scale manufacturing trials were organised with RPC, Sharpak, Færch Plast and LINPAC. The trials at LINPAC using a solid form of the ColorMatrix Dye Black-5 on APET sheet could not be completed due lack of production availability within project timescales. The following sections describe the following trials:

- Injection moulding of black PP tubs at RPC, Blackburn.
- Sheet extrusion and thermoforming of black single layer PP trays at Sharpak Yate.
- Sheet extrusion and thermoforming of black multi-layer CPET trays at Færch Plast Denmark.

5.1 Injection moulding trials of PP tubs

Commercial scale injection moulding trials using the Colour Tone IRR 95589 detectable black masterbatch were performed at RPC – Blackburn. Cream PP regrind (20%) was added to virgin PP (80%) and then coloured with the IRR colourant masterbatch at a range of concentrations varying from 0.5% to 5.0% in 0.5% increments based on the 20/80 blend.

The mixture was injection moulded into flange seal pots under standard conditions. The resulting mouldings are shown in figures 13 and 14 and they show that at least 3% of the black masterbatch was needed to mask the white pigment in the cream regrind used at 20%.

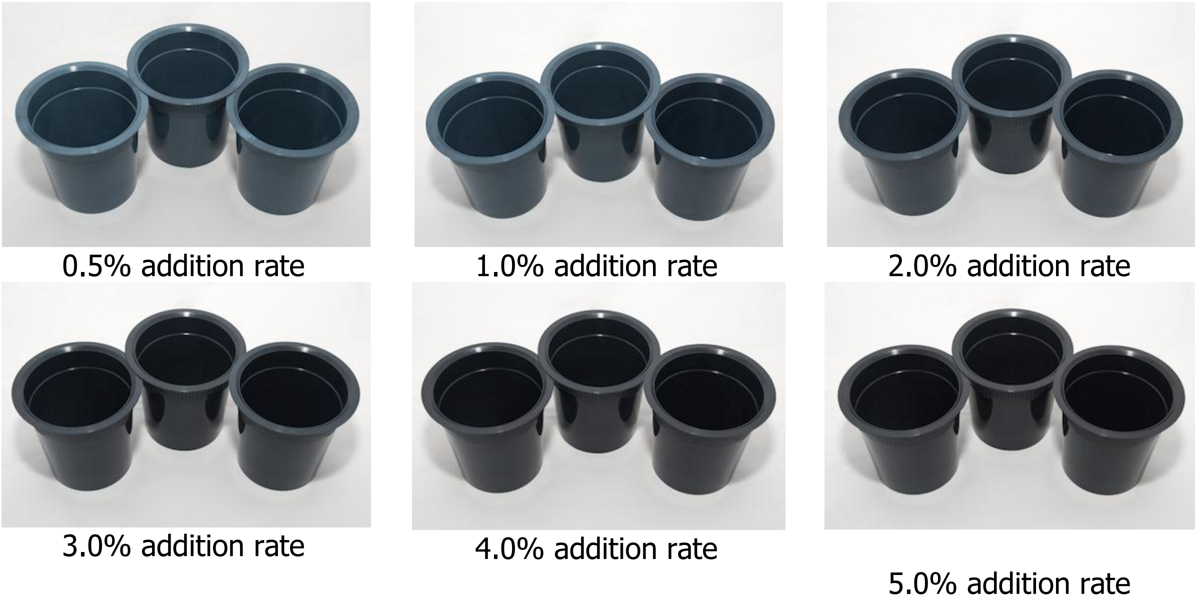


Figure 13. Example of masking performance across a range of addition rates of detectable black colourants.

Figure 14. The samples show the variation in masking strength capability of Colour Tone IRR 95589 at addition rates of 0.5% to 5.0%

These trials show that the Colour Tone IRR 95589 detectable black masterbatch needs to be used at levels of 3% or greater in order to mask the presence of 20% of cream PP regrind. Lower levels of masterbatch addition resulted in a visibly blue/green tone to the colour of the pots. This is in contrast to the performance of carbon black masterbatch that is capable of changing the same mixture of colour to a distinct black at 1% by weight. On this basis it is not recommended that cream / white coloured regrind be converted into black products to avoid the use of high addition rates of detectable black colourants that will result in increased masterbatch costs.

5.2 Sheet extrusion & thermoforming of a single layer black PP tray

Sharpak in Yate, performed trials using Colour Tone's IRR black colourant with regrind polypropylene. The aim of the trial was to mask brown regrind made up of 100% post production scrapped trays with no additional virgin or coloured PP regrind being added.

Colour Tone supplied 2Kg of (IRR 95530) black masterbatch. The addition rate for IRR 95530 was 2%. Higher levels of masterbatch were not used due to the scale of the production rate and the relatively small quantity of masterbatch available. The sheet extrusion and thermoforming trials were performed to produce a shallow vegetable/fruit tray. The results of the original colour as seen in standard production trays and the recoloured tray can be seen in Figure 15.

Figure 15. PP trays showing the influence of 2% masterbatch addition rate of the IRR 95530 detectable black colourant. Standard brown products are shown on the left and the effect of additional black is shown on the right

The results indicate that at 2% addition rate, the masterbatch was able to darken the brown colour however there was insufficient masking strength to render the tray to a shade close to black. The brown pigment in the regrind PP flakes are typically iron oxides and have proved to be very difficult to mask with this IRR 95530 detectable black.

Figure 16. Example of stacked trays showing the lack of masking achieved on the brown colour.

The tray samples indicate that even dark colours may be difficult to mask at low addition rates (i.e. 0.5-2.0%). At higher addition rates masking performance is believed to improve, however higher addition rates become more expensive. These trials show that the Colour Tone IRR 95530 detectable black masterbatch when used at levels of 2% is unable to convert the brown coloured PP regrind into a black colour. Higher levels of 3% or more may be necessary to achieve this goal with consequential increases in the cost of the formulation

Sharpak commented that in general it does not try to mix colours and rarely has the need for masking colours with carbon black. The reason for this is that it aims to use any regrind from trim/off-cuts into the same product during production and if this is not possible the material is stored until the next production run. This way the value of the coloured material is not wasted.

5.3 Multi-layer CPET sheet extrusion trials

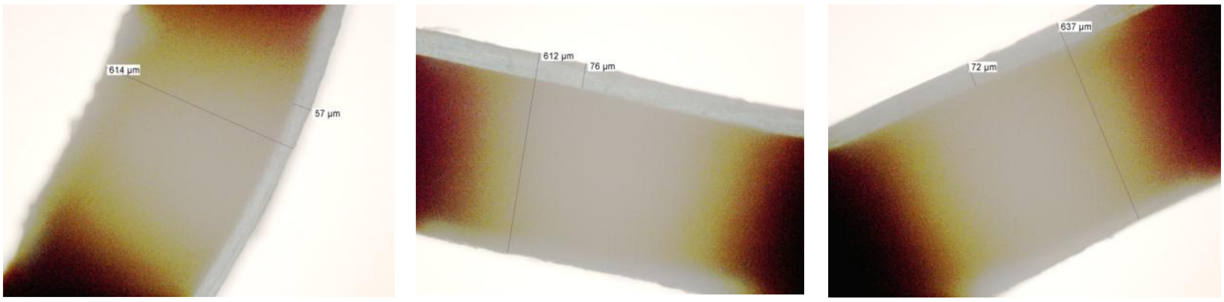
A large-scale trial was performed at Færch Plast in Denmark using the Colour Tone IRR 95591 detectable black masterbatch for CPET trays, which was a further development of the previous IRR 95559 formulation. The trial was focussed on producing two layer black CPET trays with a black surface layer and either a natural or black lower layer. There is usually a thin glossy layer of APET on the surface of CPET trays for sealability. This layer was the one being coloured with the IRR 95591 pigment. The trial involved sheet extrusion, thermoforming and a series of tests including, oven aging (crystallisation), water testing, oil test, sealing and measurement of layer thickness and colour values of trays (L, a, b values).

5.3.1 Assessment of extrusion performance

The surface appearance of the sheet was judged to be of acceptable quality by production staff at Færch Plast. The wall thickness distribution of the sheet was measured during the trial and it was found that there was a slight reduction in sheet thickness at the edge of the sheet and this was assumed to be related to a slight viscosity change.

Figure 17. Images from CPET multi-layer sheet extrusion trials at Færch Plast.

The roll used for thermoforming trials was measured to have a top layer thickness of 76micron (µm). The odour of the produced sheet was slightly different but was similar to that of the masterbatch pellets and suggests that thermal stability adjustments may be needed.



a) left roll b) mid roll used for trial c) right roll

Figure 18. Measurement of sheet layer wall thicknesses by microtome cuts to determine top layer thickness.

5.3.2 Assessment of thermoforming performance

The process remained unchanged throughout the thermoforming trials when compared to normal commercial production. Cycle times were not impacted by the use of detectable black colourants when compared to sheet containing carbon black. The trial samples were found to have similar oven stability to CPET trays containing carbon black. The sealing ability of the tray was not compromised or impacted in any way and tests found that level of sealing was acceptable for commercial production.

a) standard CPET tray masked with carbon black (LHS)

b) CPET tray masked with Colour Tone IRR at 2% in the APET top layer (RHS)

Figure 19. Example of a standard APET/CPET tray manufactured with carbon black and a two layer APET/PET tray manufactured with Colour Tone IRR 95591 NIR detectable colourant in the outer layer.

The carbon black shows more of a blue-black overtone, while the detectable black shows a more red-black colour overtone.

The trays were tested in an oven for 30 minutes at 200ºC. The colour of the trays containing the detectable black colourant led to a dull black when compared to a conventional black. This can be seen in bottom row trays in Figure 20.

Figure 20. Examples of standard (carbon black) and trial CPET trays before and after oven ageing, showing a level of greying due to crystallisation.

While both samples changed colour and became greyer in tone, the level of colour change, due to crystallisation is more evident in the tray containing the detectable black colourant. The level of colour change due to crystallisation was evaluated by measuring the tray L, a ,b values. The changes would not be visible until after a CPET tray was cooked with food and in isolation the colour shift would not be noticeable.

Table 1. Measured differences in colour change due to crystallisation when comparing a standard carbon black coloured CPET tray and a CPET tray coloured with a detectable black.

Standard CPET tray with CB	L	a	b	Trial CPET tray with DB	L	a	b
As out of tool	34.84	0.02	0.58	As out of tool	35.43	0.24	0.84
After oven test	34.95	0.11	-0.07	After oven test	36.53	0.52	-0.97
Delta	0.11	0.09	-0.65	Delta	1.10	0.29	-1.81

** where CB = carbon black; and DB = detectable black*

6.0 NIR detection assessments

TITECH GmbH in Germany performed tests on multi-layer structures from trials at Queen Mary University and also on samples produced during the large-scale trials at Færch Plast.

6.1 Results from NIR detection of multi-layer PP structures

Section 4.0 of this report describes how samples were prepared by co-extrusion. The white PP regrind was supplied by Sharpak. The detectable black masterbatch was Colour Tone IRR 95589.

- Sample 1 was a monlayer white PP layer as supplied.
- Sample 2 was a white PP layer between two layers of 70 micron LDPE coloured with 2% detectable black masterbatch.

- Sample 3 was identical to sample 2 but taken from a later part of the production run.
- Sample 4 was the same as sample 2 however the inner layer of PP was coloured with 1% carbon black.
- Sample 5 was a 200 micron monolayer of the white PP regrind with 1% of carbon black added.

The signal responses for the five samples are shown in Figure 21 and the amplified signal for sample 4 is shown in Figure 22.

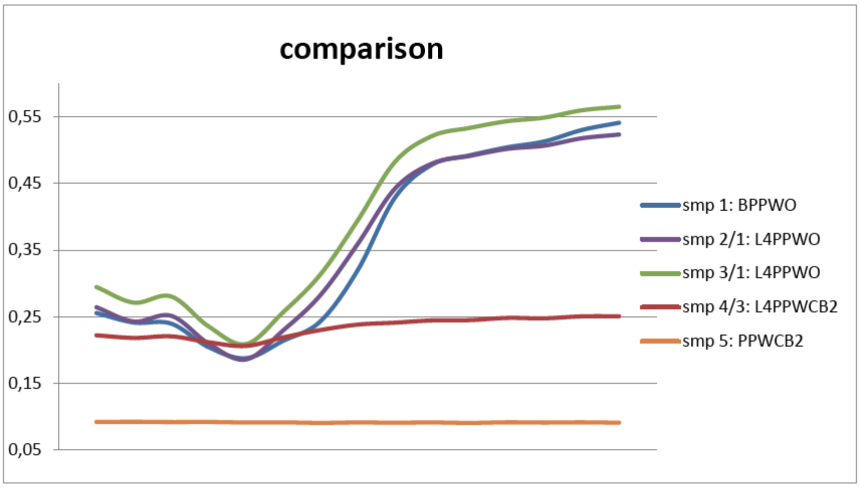


Figure 21. Detection of PP with black outer layers and white inner layer and monolayer samples in white (sample 1) and black (sample 5).

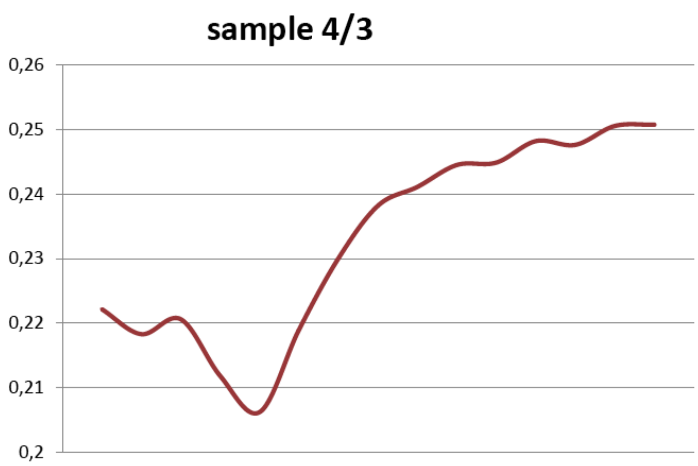


Figure 22: Enlargement of the detection signal for PP with detectable black in the outer layer and carbon black in the inner layer

The results show that the sheets with detectable black outer layer and the white mid layer (samples 2 and 3) can be readily detected as PP and have a response similar the white PP sheet (sample 1) as would be expected. The sample with the detectable black outer layers and the carbon black pigmented mid layer (sample 4) shows a lower signal strength however it can still be identified as PP. The monolayer sample of the carbon black coloured sheet (sample 5) could not be identified as expected.

These results show that the multilayer approach does work and that there is the potential to mask coloured plastics with the use of an opaque top layer with detectable black colourants, which has the potential to save on the amount of detectable black colourant used and reduce the added cost to the black sheet.

This would also mean that if any trim from trays with neutral mid layers were to be recycled, then the recyclate could be put into the top layer of other products that required the mixed coloured materials to be opacified to a black colour.

These results also indicate that the mid layer containing carbon black appears to absorb the incident infrared that penetrates below the top layer and that only the thinner top layer contributes to the spectral signature that will serve to identify the polymer as PP. This implies that the thickness and infrared absorptivity/reflectivity of this top layer will determine the signal strength going back to the detectors and will need to be taken into account if successful NIR identification is to take place.

6.2 Results from NIR detection of CPET multilayer structures

Six samples of multi-layer CPET trays were sent from Færch Plast to TITECH for testing. The front and back of the CPET trays were tested with NIR to determine the tray detectability. The trays are all shown below and were made up of a 75 micron (µm) outer layers of APET that was either coloured with 2% of Colour Tone's IRR 95591 or with carbon black (standard tray). The second layer was coloured with carbon black. The trial trays with the detectable black colourant top layers looked sufficiently black prior to crystallisation. One set of samples was oven aged and another set was oven aged with water to see if a watermark was visible after the CPET crystallisation. The samples were identified in the following way;

- Samples A, C and E used the detectable black in a 75 micron APET layer on the top and standard CPET on the base. Sample A was a tool sample, Sample C was heat treated and sample E was water/heat treated.
- Samples B, D and F used standard APET coloured with carbon black on the top and CPET on the base with carbon black. Sample B was a tool sample, sample D was heat treated and sample F was water/heat treated.

a) Detectable black 70 micron layer (front) and standard CPET (back) – standard tool sample

b) Standard APET (front) CPET (back) with carbon black – standard tool sample

c) Detectable black 70 micron layer (front) and standard CPET (back). Sample C was heat treated

d) Standard APET (front) CPET (back) with carbon black. Sample D was heat treated.

e) Detectable black 70 micron layer (front) and standard CPET(back).Sample E was water/heat treated

f) Standard APET (front) CPET (back) with carbon black. Sample F was water/heat treated.

Figure 23. Example of APET/CPET multi-layer trays produced by Færch Plast and tested for polymer detectability by TITECH.

The graphs of signal response for the front of the trays indicated a promising stronger signal for the samples with the NIR detectable black compared to the very low response for the standard trays coloured with carbon black. However the highest signal strength was approximately 4% whereas 10% is typically needed for easy identification. This means that there is an unreliably low level of polymer identification in trays manufactured with an amorphous top layer of APET and a base layer of standard CPET coloured with carbon black.

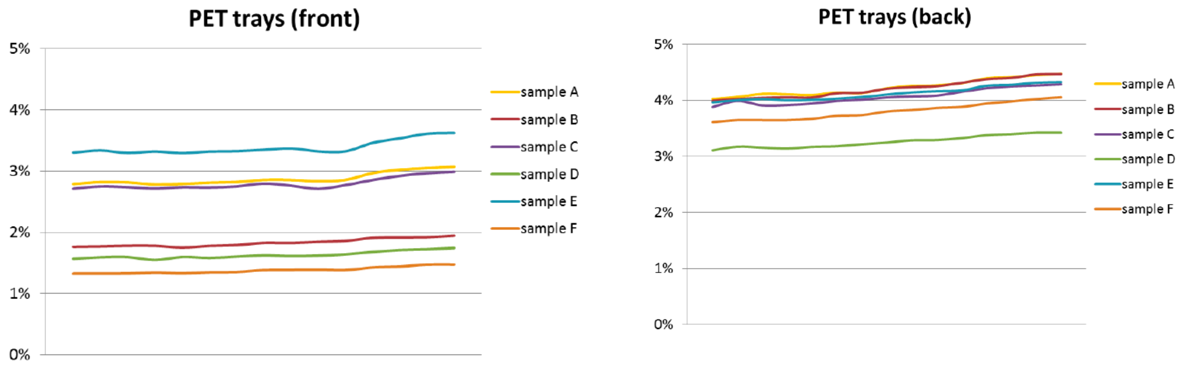


Figure 24. NIR polymer detection results for APET/CPET trays.

The results indicate that the carbon black in the base CPET layer is absorbing the main NIR signal, even with 75 micron (µm) detectable black APET top layer. The NIR signal from the top layer is present however it is not strong enough to allow reliable detection at that thickness . The APET layer seems to be relatively transparent to the incident infrared allowing most of the infrared to be absorbed by the lower layer of carbon black coloured CPET.

At this point it is useful to consider why the PP multiplayer sheet with the carbon black mid layer could be identified yet the comparable APET/CPET combination could not be identified.

It appears that the reason could be linked to the level of crystallinity and/or the infrared reflectivity/absorptivity of the top layer of the sheet. Crystallinity increases density and will improve the infrared reflectance of the polymer layer.

In the case of the PP multilayer sheet, the PP top layer is predominantly crystalline whereas the top APET layer would not be highly crystalline even after a heat treatment due to the way the material is intentionally formulated to be amorphous. Therefore in the case of APET/CPET construction, the reflection of the NIR signal from the top layer to the sensor detector could be too low to allow for reliable polymer identification.

Figure 24 showed the strength of signals from APET/CPET trays is low (less than 5%) and below the threshold of 10% that TITECH consider to be required for identification under industrial conditions.

The tests conducted to date suggest that the presence of carbon black under a layer of APET may make the APET undetectable. The identification of the trays could be improved by making the top layers thicker and by increasing the reflectivity of the top layer with other non-black additives so that a stronger signal would be generated to allow polymer identification.

Overall the multilayer tests showed that the use of detectable black colourants in an outer layer could be used to opacify a mixture of colours in the mid layer and permit successful high speed polymer identification. While it would be tempting to add carbon black to the mid layer to reduce the level of opacity required in the outer layer, it has been shown that the strong absorptivity of the carbon black will interfere with the identification of the polymer in the outer layer and that further tests would be need to prefect this approach.

7.0 Conclusions and recommendations

The masking strength trials show that NIR detectable black colourants have poor masking properties when compared to carbon black pigment at typically used addition rates of 1-2%. Detectable black colourants show that they can effectively mask a variety of colours but the masking is only achieved at higher addition rates of 3-5%. Due to the high cost of NIR detectable colourants, masking with detectable black colourants would not be economically viable for converters.

Discussions with convertors identified that very few convertors actually mix colours. This is because once colours are mixed the value is typically lost and for this reason the off cuts and trims are typically used as regrind directly during production, and colour masking is not required. Consequently the lower masking performance of detectable black colourants may not be a significant disadvantage and may not prevent them from being used in commercial products. It means that the detectable black colourants may be used without further development.

The approach of using multi-layer structures has the potential to provide an alternative method for masking a variety of colours which may also reduce the cost of sheet by using carbon black in the middle layer and the detectable black colourants only in the outer layers. Tests conducted on PP multi-layer structures showed that the sheet could be identified by the top 'cap' layer polymer, even when the middle layer is coloured with carbon black. Further work is needed to confirm if the same result can be obtained for APET/CPET product detection. This should include other spectroscopic means of detecting the surface or by improving the reflectance in the detectable black colourants. If this approach is successful then the mid layer could be used to accept plastics that contain carbon black and the top layer would have reduced masking requirements.

Further research into improving the masking strength of both pigment based and dye based detectable black colourants is likely to be continued by the colourant suppliers. Using one or other of the two different colourant systems may offer advantages in some polymers and those products will be of interest to converters because a higher masking strength will allow less colourant to be used to make the use of these detectable black colourants more economic.

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