Near infrared hyperspectral imaging applied to recycling of postconsumer polyolefins

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Introduction

Polyolefin (PO) recovery from plastic solid waste (PSW) is considered a great opportunity and a big challenge, as PO makes up more than one third of the total plastics consumption in Europe but is the least recycled plastic due to difficulties in separation.¹ There are many sources of PO-rich complex waste, such as construction and demolition (C&DW), electric and electronic equipment (WEEE), automotive shredder residue (ASR) and household waste (HW). In recycling technologies of plastic from post-consumer waste, the capability to separate different polymers is one of the key points in order to obtain pure secondary raw materials for the production of new high quality products. In this paper, the use of NIR hyperspectral imaging (HSI) was applied to the classification of plastic materials coming from B&CW, in order to control the quality of products that result from an innovative recycling process based on Magnetic Density Separation (MDS).² An MDS recycling process is under development in the framework of a European FP7 Project entitled "W2Plastics: Magnetic Sorting and Ultrasound Sensor Technologies for Production of High Purity Secondary Polyolefins from Waste". The recycling project will include the development and implentation³ of online quality control logics for the process feed (i.e. complex plastic waste streams) and for the final products resulting from the sorting process.

Polyolefins characteristics and recycling

Polyolefins are the largest group of thermoplastics; the term polyolefins means "oil-like" and refers to the oil feel that these materials have.⁴ They consist only of carbon and hydrogen atoms and they are non-aromatic. The two most important and common POs are polyethylene (PE) and polypropylene (PP) and they are very popular due to their low cost and wide range of applications.

PE is probably the most diffused plastic in the world. It is a very versatile material that makes grocery bags, shampoo bottles, children's toys and even bullet-proof vests. Although it has a wide field of application, PE has a very simple structure (the simplest of all commercial polymers) consisting of long chains of the monomer ethylene. A molecule of PE is thus a long chain of carbon atoms with two hydrogen atoms attached to each carbon: [CH₂-CH₂]_n. This type of PE is called linear PE or HDPE (high density polyethylene) because the carbon chain does not have any branches. Sometimes some of the carbons are attached to long chains of PE instead of hydrogen atoms. This is called branched PE or LDPE (low density polyethylene). The branching of these short and long chains causes the chains to not pack into the crystal structure. Therefore LDPE has a lower density and weaker intermolecular forces than HDPE.

PP is a rather versatile polymer, serving both as a plastic and as a fibre. PP plastics are used to make things like dishwasher-safe food containers and PP fibre is often used to make indoor-outdoor carpeting (PP is easily pigmented and is water resistant). PP is a vinyl polymer with a linear structure based on C_nH_{2n} . The structural similarities between PP and PE are limited: every other carbon atom in the backbone chain has a methyl group attached to it. Most commercial PP has a level of crystallinity intermwdiate between that of LDPE and HDPE.

Separation of PO is not easy with conventional technologies based on sink and float strategies due to the narrow range of densities: $\delta_{\text{HDPE}} = 0.940 - 0.960 \text{ g/cm}^3$, $\delta_{\text{LDPE}} = 0.910 - 0.935 \text{ g/cm}^3$, $\delta_{\text{PP}} = 0.880 - 0.915 \text{ g/cm}^3$. Currently available techniques, based on the difference in flotation properties in water, can be used to separate lighter types of plastic such as PO from the heavier types such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC). The resulting PO mixture can only be used to produce low-quality recycled objects as it no longer possesses the physical and mechanical properties characterising the virgin polymers. To produce high-purity granulates from these concentrates; the mixture must be sorted very accurately to obtain two pure separate products: PP and PE.

Among different techniques under study or available in the market,^{6,7} MDS appears to be a valid solution for PO recycling.⁸ MDS uses a highly dilute mixture of water and ferrous oxide (nanometre sized ferrite particles) in a magnetic field. Such liquids derive their separation density from a combination of a magnetic

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Figure 1. PO-C&DW source waste sample.

Figure 2. Example of 9 selected plastic particles of different colours from 0.89–0.90 g.cm⁻³ density class.

field and gravity. A magnetic field, applied to the magnetic liquid, produces a density gradient inside the fluid allowing the separation of particles with apparent density lower than water. An intriguing property of MDS liquids is that they have different separation densities in different layers of the fluid, as determined by different intensities of the magnetic field. In principle, this effect can be used to separate a complex mixture into many different materials in a single process step using the same liquid. Other important advantages linked to MDS liquids (composed of 99% water and 1% iron oxide) are that; i) they are environmentally harmless⁹, in fact they can be used without the economic and environmental problems of organic liquids, and ii) that they are very cheap to use, even if not fully recovered from the product materials.

Independently of the adopted separation strategy, the need to operate a full quality control of the plastic waste streams represents a key issue of great importance for both plastic recycling and compounder industries. Therefore, a fast online assessment to monitor the plastic waste feed streams and to characterise the composition of the different PO products is fundamental to increase the value of secondary PO.

The current evaluation of PO waste purity, in terms of the concentrations of PE, PP and non-polyolefin contaminants, is carried out by hand-sorting and differential scanning calorimetry (DSC) analysis of samples in a laboratory. Other methods of analysing waste stream outputs include crystallisation analysis fractionation (CRYSTAF), attenuated total reflectance Fourier transform infrared (FTIR-ATR) spectroscopy and temperature rising elution fractionation (TREF).

Materials and Methods

Samples

A mixed PO sample from C&DW (Figure 1) has been collected in a recycling facility located in France. The sample is constituted of shredded particles ranging in size from 5 to 20 mm representing the float fraction $(\text{density} < 1 \text{ g.cm}^{-3})$ of a sink-float pre-processing step, i.e. mainly PO, as the other polymers are characterised by densities greater than that of water (1 g.cm⁻³). The sample was classified into 9 different density fractions from several sink-float separation stages, i.e. using the static bath method with various water and water-ethanol mixtures at room temperature. The selected density intervals were typical of PP and PE and ranged from <0.88 g.cm⁻³ up to 0.96 g.cm⁻³ (Table 1). Plastic particles of different colours have been selected from the 9 density classes, identifying 9 main colours (Figure 2): transparent, white, pink, red, orange, grey, blue, green and yellow. Black particles have not been taken into account at this stage of the research due to their poor reflectance characteristics. 18 particles have been selected for each density class, 2 for each of the 9 dominant colours, for a total of 162 particles.

Virgin PP and PE samples (Figures 3 and 4) have been utilised as reference standards for the recognition of the unknown waste PO particles based on their spectral signatures.¹⁰

Density Class (g.cm ⁻³)	<0.88	0.88–0.89	0.89–0.90	0.90–0.91	0.91–0.92	0.92–0.93	0.93–0.94	0.94–0.95	0.95–0.96
Weight (g)	58.13	85.79	103.06	131.00	62.05	79.00	136.70	83.07	106.02

Table 1. Density classes and related weights of the analysed PO mixed sample coming from C&DW waste.

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Figure 4. Pure PE plastic sample

Figure 3. Pure PP plastic sample

Laboratory set up, spectral acquisition and analysis

The acquisition system (Figures 5 and 6) was a NIR spectral camera (Specim, Finland), consisting of an ImSpector N17E imaging spectrograph working in the 1000–1700 nm wavelength region and a temperature stabilised InGaAs camera. It works as a push-broom type line scan camera providing full, contiguous spectral information for each pixel in the line. The spectral camera is hosted in a laboratory platform developed by DV srl (Italy) to perform the inspection of different samples. The platform is equipped with a conveyor belt for positioning particles to be acquired, a frame to hold the spectral sensor and light source, a control console used also as working table, and a place for a computer and monitor. The device is fully controlled by a PC unit equipped with the Spectral Scanner[™] v.2.3¹¹acquisition/preprocessing software.

Reflectance spectra in the 1000 - 1700 nm wavelength range were acquired with a spectral resolution of 7 nm; a total of 121 wavelengths were measured. The spectrometer was coupled to a 50 mm lens; image width was 320 pixels while the number of frames was 280.

Three spectral pre-processing steps were used, summarised as baseline, derivative and mean centering. Baseline pre-processing reduced the amount of redundant data and decreased the leverage of outliers. Derivative pre-processing emphasised the spectral ranges with high levels of characterising information. Mean centering stressed the spectral deviation of samples. Principal component analysis (PCA) was applied after data pre-treatment to classify PO samples into two classes (PP and PE) using the PLS Toolbox (Version 6.0.1, Eigenvector Research, Inc.) running inside Matlab[®] (Version 7.11.0, The Mathworks, Inc.).

After pre-processing procedures, data were split into a calibration dataset and a validation dataset, and used to create a robust prediction model. Finally, the number of parameters (principal components for PCA) used to build the model was chosen based on fast computing and best performance.

To validate the classification results obtained by PCA on HSI data, the same unknown plastic particles were classified by Raman spectroscopy using a DeltaNu Advantage 785[™] benchtop Raman spectrometer equipped with a NuScope[™]. The Advantage 785 utilised a 120 mW (80 mW at sample) and 785 nm diode laser. The investigated spectral range was 200–2000 cm⁻¹ with a spectral resolution of 5 cm⁻¹.

Results and Discussion

In Figure 7, the reflectance spectra acquired by HSI in the NIR range (1000–1700 nm) are reported, showing the typical spectral response for virgin PE and PP samples, and for a PE and a PP waste plastic particle.

The most important spectral regions for distinguishing PE and PP were the CH overtone regions around 1150-1250 nm, 1350-1450 nm and 1650-1750 nm and an unassigned region at 1500-1550 nm.

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Figure 7. Reflectance spectra of typical PE and PP particles, both virgin and from waste, acquired by the hyperspectral system in the NIR range (1000-1700 nm). The shadowed regions indicate the wavelengths at which the two polymers are more easily identified.

An interesting feature in the spectral signatures of PP and PE, useful for recognition of the two polymers, is that the reflectance levels of PP are higher on average than those of PE. This is probably due to the surface properties of the two POs, with PP being shinier than PE.

The results of PCA applied on the average spectral signatures of PP and PE particles are shown in Figure 8. From the PCA score plot, factor 1 (PC1) and factor 2 (PC2) explain 81.48 and 16.07% of variance, respectively. The two kinds of PO are clearly discriminated along PC2, with mainly positive values for PP particles and negative values for PE particles. Comparing the results with those obtained by Raman spectroscopy, all the particles have been correctly classified as PP (green stars) and PE (red triangles).

Based on the classification results obtained by HSI it has been possible to obtain the frequency distribution of PP and PE in each density fraction (Figure 9). PP was concentrated in the lowest density classes (from <0.88 to 0.90–0.91 g.cm⁻³) whereas PE was concentrated in the highest density classes (from 0.91–0.92 up to 0.95–0.96 g.cm⁻³). The cut-off density between PP and PE was identified as 0.91 g/cm³, in agreement with the theoretical density interval characteristics of the two POs.

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Figure 8. PCA score plot for C&DW plastic particles based on HSI spectral signatures in the NIR wavelength region 1000–1700 nm.

Defining the density cut-off between the two POs is particularly useful for the tuning of the MDS process and for understanding the behaviour of PO particles inside the magfluid.

The HSI classification results were also used to characterise differently coloured PP and PE particles (Figure 10). The best segregation between similarly coloured PE and PP particles was observed with transparent and brown particles (mostly PE), and white and pink particles (mostly PP). The characterisation of colour distribution between the two POs can be useful for better addressing quality control strategies based on optical and spectroscopic sensing techniques.

Our results demonstrate that the adopted HSI approach provides information useful for the design and implementation of innovative quality control in PO recycling plants. An efficient quality control strategy must be robust, fast and simple, while also being low cost and allowing high production rates; all these requirements can be satisfied adopting an HSI approach.



Figure 9. Frequency distribution of PP and PE particles for each density fraction. The cut-off density of 0.91 g.cm⁻³ between the two POs was identified.



Figure 10. Distribution of PP and PE (% in number of particles) among the 9 different colour classes.

Conclusions

New analytical inspection strategies based on hyperspectral imaging in the NIR field (1000–1700 nm) have been investigated and set up. The HSI-based strategy will be used to define quality control logics that could be profitably applied in online architectures at industrial plants for PO recycling. The HSI technique has been applied in order to identify PP and PE from complex waste streams constituting the feed of an innovative separation approach based on MDS.

PE and PP products were selected on the basis of their density and colour by multi-stage-densityseparation. HSI provided a method for recognising different density classes and colours of materials. Further investigations will be carried out to evaluate the possibility of classifying darkly coloured or black particles (i.e. particles with poor reflectance properties).

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