

Post-Consumer Polyolefins (PP-PE) Recognition by Combined Spectroscopic Sensing Techniques

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Abstract: The efficient large-scale recycling of plastic waste is of increasing interest from an ecological and economic point of view, but it represents a goal that has yet to be achieved by the recycling industry. The possibility offered by different spectroscopic sensing techniques in order to identify different plastic particles to be recycled, with particular reference to polyolefins from complex wastes, has been investigated. Representative samples of polyolefins (polyethylene and polypropylene) have been collected and analyzed for laboratory set-up and testing by FT-IR spectroscopy, by Raman spectroscopy and by hyperspectral imaging in two different wavelength fields, 400-1000 and 1000-1700 nm, respectively. The spectral signature obtained by the different techniques of the two plastic typologies have been detected, analysed and compared. The main parameters that allow to perform the recognition of the polyethylene (PE) and polypropylene (PP) have been defined, with particular reference to the hyperspectral imaging innovative technique. The analytical strategies can be utilised to define sorting and/or control logics to be applied in "on-line" control architectures to directly act at industrial plant level.

Keywords: Recycling, secondary plastics, polyolefins, hyperspectral imaging, FT-IR spectroscopy, Raman spectroscopy, sorting.

1. INTRODUCTION

Plastics are continuously replacing other materials in a number of applications. From greenhouses, mulches, coating and wiring, to packaging, films, covers, bags and containers. It is only reasonable to find a considerable amount of Plastic Solid Waste (PSW) in the final stream of Municipal Solid Waste (MSW). In the EU countries, over 250×10^6 t of MSW are produced each year, with an annual growth of 3%. In 1990, each individual in the world produced an average of 250 kg of MSW generating in total 1.3×10^9 t of MSW [1]. Ten years later, this amount almost doubled levelling at 2.3×10^9 t. In the United States, PSW found in MSW has increased from 11% in 2002 [2] to 12.1% in 2007 [3]. Increasing cost and decreasing space of landfills are forcing considerations of alternative options for PSW disposal [4]. Years of research, study and testing have resulted in a number of treatment, recycling and recovery methods for PSW that can be economically and environmentally viable [5]. The plastic industry has successfully identified workable technologies for recovering, treating and recycling of waste from discarded products. In 2002, 388.000 t of polyethylene (PE) were used to produce various parts of textiles, of which 378.000 t were made from PE discarded articles [6].

PSW treatment and recycling processes could be allocated to four major categories [7]: i) re-extrusion (primary), ii) mechanical (secondary), iii) chemical (tertiary) and iv) energy recovery (quaternary). Each method provides a unique set of advantages that make it particularly beneficial

for specific locations, applications or requirements. Mechanical recycling (i.e. secondary or material recycling) involves physical treatment, whilst chemical recycling and treatment (i.e. tertiary encompassing feedstock recycling) produces feedstock chemicals for the chemical industry. Energy recovery involves complete or partial oxidation of the material [8], producing heat, power and/or gaseous fuels, oils and chars besides by-products that must be disposed of, such as ash.

Among PSW, polyolefins represent a very important family of polymers, constituting more than a third of the total plastics consumption in Europe, but they are the least recycled plastic materials, as a consequence polyolefins waste recovery represents one of the major opportunities in PSW recycling. The two most important and common polyolefin's are polyethylene (PE) and polypropylene (PP) and they are very popular due to their low cost and wide range of applications. Only one million t out of 14 million t yearly sold in Europe is being recycled and complex wastes provide the vastest, presently unused potential resource of secondary polyolefin. Actually, polyolefin recyclers focus mainly on the relatively pure post-industrial or single-product wastes, since these wastes can be made into high-purity product materials by existing and cost-effective process technology. Post-industrial wastes are increasingly exported outside the EU, however, and so the polyolefin recycling industry and their end-users are forced to look for alternative resources. In principle, post-consumer wastes, such as Waste from Electric and Electronic Equipment (WEEE), household waste and Automotive Shredder Residue (ASR) provide such a resource [9]. They are a five to ten times larger reservoir of polyolefin than do post-industrial wastes, but these wastes are also much more

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complex mixtures of materials and hence much more difficult to recycle. Technologies that are to address these resources need to be extremely powerful, since they must be relatively simple to be cost-effective, but also accurate enough to create high-purity products and able to valorize a substantial fraction of the materials, present in the waste, into useful products of consistent quality in order to be economical. On the other hand, the potential market for such technologies is large and the boost of environmental regulations, and the oil price increase, has made many industries interested both in waste sorting technologies, for the production of high quality secondary polyolefins, as well as in developing automatic sensors for quality assessment of polyolefin products. This latter aspect is particularly crucial because: “no matter how efficient the recycling scheme is, sorting is the most important step in recycling loop” [10]. A fast, accurate and reliable identification of the primary plastics and the polluting materials in the feed is thus essential to set up suitable mechanical actions on PSW and optimal sorting strategies on the resulting products. The attainment of this goal is thus fundamental for companies that buy recycled plastics, because they obviously want that those recycled plastics have the same characteristics as virgin ones. Otherwise, it is not efficient, and sometimes dangerous, to use recycled plastics materials. A simple example is the case of polyethylene terephthalate (PET) and polyvinylchloride (PVC), which are sometimes indistinguishable by sight. These two resins are contaminants to each other. Combinations of PVC and PET resins can result in the release of hydrochloric gases. The PET resin will be ruined even with only a few parts per million of PVC resin.

In this paper the possibility offered by different spectroscopic sensing techniques have been investigated and evaluated with reference to their sorting, that is the possibility to utilize *HyperSpectral Imaging* (HSI), FT-IR spectroscopy and Raman spectroscopy to preliminary identify *polymers-pieces* spectral firms and to define further *on-line* sorting strategies. More specifically such an approach was developed inside the European FP7 Project

W2P - *Magnetic Sorting and Ultrasound Sensor Technologies for Production of High Purity Secondary Polyolefins from Waste*. Aim of this project was to identify and separate polyolefins (PP-PE) from the other contaminants, plastics and not, present both in the feed (quantitative quality assessment of the plastic waste materials to process) and in the different flow streams (process quality control) resulting from an innovative approach based on Magnetic Density Separation (MDS).

2. POST CONSUMER PLASTICS SORTING: A QUICK OVERVIEW

Despite the strong technological development most of the current plastic sorting continues to be done by hand. *Manual sorting* is a simple process that needs very little technology. It is a very labour intensive, costly and inefficient method for sorting materials and more specifically plastics. For this reason, the Society of the Plastics Industry instituted a voluntary labelling system. The system created a set of codes (Table 1) for each of the six most commonly used resin types. Even with this labelling system, it is still difficult to manually distinguish polymer types due to the condition of the plastics as they reach the separation facility. Plastic containers, in fact, may be crushed, cracked or covered rendering the resin label practically useless. In these last years a lot of automated sorting strategies have been investigated, developed and implemented, they can be divided in two categories according to the size of plastics object to sort, that is: *macro-sorting* and *micro-sorting*. The first one (*macro-sorting*) deals with the separation of bottles or containers, as a whole. Such an approach as the advantage, needs very little or no preparation before sorting. The second one (*micro-sorting*) deals with plastic materials after they have been milled up into pieces. This system has the advantages of lower handling costs and larger volume processing; but a more sophisticated technology is required.

2.1. Macro-Sorting

Plastic *macro-sorting* is addressed to separate plastics manufactured good as recovered after their use. Strategies

Table 1. Example of Most Common Type of Plastics and Use

	PET	Polyethylene terephthalate - Fizzy drink bottles and oven-ready meal trays.
	HDPE	High-density polyethylene - Bottles for milk and washing-up liquids.
	PVC	Polyvinyl chloride - Food trays, cling film, bottles for squash, mineral water and shampoo.
	LDPE	Low density polyethylene - Carrier bags and bin liners.
	PP	Polypropylene - Margarine tubs, microwaveable meal trays.
	PS	Polystyrene - Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
	OTHER	Any other plastics that do not fall into any of the above categories. An example is melamine, which is often used in plastic plates and cups.

have to be thus addressed to recognise big targets. The main problem to face, following this approach, is to set up a suitable processing line able to handle large pieces and consequently large and cumbersome stocks. Different techniques have been investigated in the past years and are currently utilised, that is:

- near-infrared spectroscopy,
- X-rays analysis,
- laser aid identification,
- marker systems.

Near-infrared spectroscopy. This techniques is one of the most utilised to perform an automated sorting of post-consumer plastic containers. It is based on the energising of the unsorted, unidentified plastic with near-infrared waves (600-2500 nm). When the infrared light reflects off the surface of the plastic, the different resin's characteristic infrared absorption bands can be measured. The detected bands are then compared to known polymer spectral bands response, in the same wavelength range, to determine the plastic type. Such an approach is characterised by many advantages. The most significant one is the detection/identification speed. Because of the great scanning speed allowed by spectroscopic devices, many readings of one sample can be taken in short periods of time; a multiple check of the same object is thus possible allowing to set-up proper and reliable identification strategies. Detection speed also allows an increased volume of plastics sorted in smaller amounts of time. The second advantage is the lack of specimen preparation. Labels, or other obstructions like dirt, thanks to the possibility to perform multiple checks, do not significantly interfere with readings. Finally this detection architecture present another advantage: colour do not interfere with proper resin identification. Except for black, the readings are independent of the colour of the resin. Black containers represent a problem, being their colour a strong absorber in the near-infrared region. As a result black plastic produces a featureless spectrum that, in many cases, does not allow a proper identification [11].

X-rays analysis. This sorting approach is based on the study of the transmitted or reflected wavelengths in the X-ray region. This technology is mainly applied for PVC sorting. Chlorine atoms in PVC, in fact, give a unique peak in the X-ray spectrum that is readily detectable.

Laser aid identification. Following this approach the detection architecture identifies plastics by shining a laser beam onto the surface to be identified and then analyzing the material's response. Utilising an infrared thermographic system, various material properties including absorption coefficient, thermal conductivity, thermal capacity, and surface temperature distribution can be thus determined. The detected properties can then be analyzed to identify plastic type. The resulting system is suitable for quick analysis and identification of various plastics. The proposed approach presents some advantages, that is: i) different thickness, forms, and surface structures of plastics containers do not play any role in the identification and ii) printing and different additives (softeners) also do not play any role. The limits being linked to: i) presence, in terms of quantity and quality (particularly of carbon) of fillers, ii) difficulty in

classification of plastics due to the evaluation of the maximum temperatures directly after laser radiation and, as a consequence of i) and ii), a lower identification speed, in comparison with spectroscopy and X-ray: plastic containers check can be carried out within *only* in 1/10 s.

Marker systems. This approach entails marking either the container or the resin itself with something readily detectable. There are seemingly no insurmountable barriers standing in the way of an automated sorting system that would read a hidden marker and identify resin type. Lot of studies and attempts have been carried out in the '90s, but with low success, mainly for the problems arising both at production and recycling level. Every packaging production line should have to install a marking system on their line. Also, each recycler would need to install a machine to scan for the marking on the containers.

2.2. Micro-Sorting

Plastic *micro-sorting* is addressed to separate post-consumer plastics after a combination of comminution/separation processes specifically addressed to remove contaminants (e.g. non plastic materials) and reduce the "apparent" volume of plastic to manipulate. Following this approach sorting has to be faced in a different way that is a process phase inside a complex physical-mechanical handling-separation lay out. Differently from *macro-sorting*, in *micro-sorting* the target to sort is just a small flake. Processing speed has thus to be high in order to realise a valuable recycling. To fulfil this goal different techniques are currently utilised, that is:

- sink and float process,
- flotation,
- selective dissolution and flash devolittisation.

Sink and float process. Sink and float separation systems are very common. They represent a simple and robust approach to separate materials characterised by different densities. The method simply involves depositing the materials in a tank filled with water or other liquid at a specific density. The lighter materials float and the heavier ones sink. For a sink and float system to work efficiently the materials' densities must differ greatly from one another. These methods are not particularly helpful, because most plastics are very close in density ($\rho_{HDPE} = 0.941 \text{ g/cm}^3$, $\rho_{MDPE} = 0.926\text{--}0.940 \text{ g/cm}^3$, $\rho_{LDPE} = 0.915\text{--}0.925 \text{ g/cm}^3$, $\rho_{LLDPE} = 0.910\text{--}0.940 \text{ g/cm}^3$, $\rho_{PP} = 0.960 \text{ g/cm}^3$).

Flotation. Froth-flotation is another possible method to utilise to perform plastics *micro-sorting*. Flotation works very similar to sink and float systems. Plastic waste to separate are preliminary conditioned with a surfactant and then suspended in water. Due to the conditioning some plastics, that normally sink (hydrophilic behaviour), adhere, according to their composition, to air bubbles generated by a controlled air flow pumped into the system. As a result such a particles float to the surface. Materials that are not affected by the bubbles sink to the bottom. Collection systems at the top and bottom of the system can then recover the separated fractions.

Selective dissolution and flash devolittisation. Selective dissolution and flash devolittisation is a plastic sorting option

that was in depth investigated, as the markers for macro-sorting purposes, in the early 90's. The process separates mixed or commingled plastics waste into nearly pure reusable polymers without any mechanical pre-sorting techniques. These technologies are not cost-effective for commodity polymers, but are sometimes the only solution for the liberation of different coatings associated with PP, such as paint or skin.

3. POLYOLEFINS (PE-PP) SEPARATION

A number of techniques have been developed in order to separate and sort PSW [12] containing polyolefins. In the recycling industry, sorting and identification must be attempted within a short time to positively affect a recycler's finances. Both fast and accurate identification of the primary plastics contained in a particular item, followed by some type of manual or automated sorting are essential. In the case of plastic bottle sorting, as outlined in the previous paragraph, automated techniques do exist but some times are not so easy to implement due to a difference in shape and size of the containers and/or the existence of paint and coating which delays the analysis technique, etc. Different processing layouts have been thus proposed based on different separation technologies, most of them embedding, even if not particularly efficient, density sorting. Also this latter approach is not particularly efficient. To enhance the effectiveness of density separation, hydrocyclones are commonly used. Hydrocyclones, which use centrifugal force, enhance material wettability. Some of the factors affecting liquid separation of a given material are its wettability, its variation in density (porosity structure, fillers, pigments, etc.), shape factors of size-reduced particles, and its level of liberation from other material. Even surface air bubbles, which can attach to plastics as the result of poor wetting or surface contamination, can cause an individual flake of material to float in a solution less dense than that of bulk material [13]. A powerful alternative to "classical" density separation techniques is represented by MDS combined with a new innovative classes of optical sensing devices able to perform: i) an *on-line* control of the fed plastics waste streams, ii) a quality control of the products (PP and PE) resulting from processing, specifically from MDS, and iii) to be also utilised as sensing/detection unit for PP and PE *micro-sorting*. Innovative HSI devices and related detection logics have been investigated and compared with the classical ones, based on FT-IR and Raman spectroscopy, in order to develop and implement HSI based *on-line* micro-sorting devices able to combine the information related to materials surface spectral characteristics, in the visible (VIS) and in the near-infrared (NIR) wavelength ranges, and their pictorial attributes.

4. SPECTROSCOPIC SENSING TECHNIQUES FOR POLYOLEFINS IDENTIFICATION

4.1. FT-IR Spectroscopy

Infrared (IR) spectroscopy is a chemical analytical technique, able to determine the IR intensity versus wavelength of light. Based upon the wave-number, IR light can be categorized as near infrared ($4.000-14.000\text{ cm}^{-1}$), Mid IR ($400-4.000\text{ cm}^{-1}$) and Far IR ($4-400\text{ cm}^{-1}$). IR spectroscopy allows collecting information related to the vibration characteristics of chemical functional groups in a

sample. When an IR light interacts with the material, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb IR radiation in a specific wave number range independently from the remaining structure of the molecule. The possibility to establish a correlation between band wave-number and chemical structure allows identifying a functional group inside the sample. Such correlation related to wave-number positions where functional groups adsorb, are practically independent from effects related to: sampling strategy, pressure and temperature conditions, possible change of the molecule structure in other region of the molecules. The presence of specific functional groups can be monitored by these IR infrared bands. FT-IR spectroscopy is based on a Fourier Transform Infrared (FT-IR) spectrometer able to obtain an infrared spectrum in two steps, that is: i) collecting an interferogram of a sample signal with an interferometer, which measures all of infrared frequencies simultaneously and ii) utilising an FT-IR spectrometer to acquire and digitise the interferogram, performing the FT function and producing as output the spectrum.

4.2. Raman Spectroscopy

Raman spectroscopy is a powerful technique particularly suitable to perform chemical analysis due to its unique advantage over other analytical techniques, being a non invasive and non destructive method. It allows to obtain materials fingerprint spectrum. No sample preparation is required. Another advantage of Raman spectroscopy is that not a larger amount of sample is required for the analysis. Furthermore, a short amount of measuring time, normally a few seconds, is required to obtain a Raman spectrum, this represents a big advantage making possible a real time monitoring of chemical reactions. A standard Raman analytical device is commonly composed by four elements: i) the energizing source, ii) the collection device, iii) the spectrograph and iv) and the signal processing architecture. With reference to plastic materials characterisation, Raman spectroscopy can be profitably utilised: i) in real-time monitoring of polymerization reactions to control the processing time, quantitative compositional analysis, of polymer melt streams, and ii) in waste plastic characterisation in the recycling sector, especially for PP and PE identification.

4.3. Hyperspectral Imaging

Imaging spectroscopy is based on the utilization of an integrated hardware and software architecture able to digitally capture and handle spectra, as an image sequence, as they results along a pre-defined alignment on a surface sample properly energized. According to the different wavelength of the source and the different spectral sensitivity of the device, different physical-chemical superficial characteristics of the sample can be investigated and analyzed. The imaging based spectroscopy strategy, adopted in this study, is based on the utilization of a device belonging to the ImSpectorTM series spectrometer, developed by SpecImTM Oy. The spectrograph is constituted by optics based on volume type holographic transmission grating [14]. The grating is used in patented *Prism-Grating-Prism* construction (PGP element) characterized by high diffraction efficiency, good spectral linearity and it is nearly free of

geometrical aberrations due to the on-axis operation principle. A collimated light beam is dispersed at the PGP so that the central wavelength passes symmetrically through the grating and prisms and the short and longer wavelengths are dispersed up and down compared to central wavelength. This results in a minimum deviation from the ideal on-axis condition and minimizes geometrical aberrations both in spatial and spectral axis. The result of acquisition is constituted by a digital image where each column represents the discrete spectrum values of the corresponding element of the sensitive linear array. Such an architecture allows, with a “simple” arrangement of the detection device (“scan line” perpendicular to the moving direction of the objects) to realize a full and continuous control. Line lighting, as energizing source with uniform spatial distribution, was used. Calibration was performed in three steps: i) spectral axis calibration with spectral lamps; ii) dark image acquisition and iii) measurements of “white reference image”. After the calibration phase: i) the image spectra is acquired and ii) the reflectance (R_{ci}) (at wavelengths i and spatial pixels c of interest) is computed:

$$R_{ci} = \frac{[(sample)_{ci} - (dark)_{ci}]}{[(white)_{ci} - (dark)_{ci}]} \quad (1)$$

Such a procedure enables to compensate the offset due to CCD dark current and separates the sample reflectance from the system response.

5. MATERIALS AND METHODS

The investigated samples are virgin granules and tablets of LDPE, HDPE and PP polymers, as listed in Table 2.

Table 2. List of the Analysed Polyolefins Sample

Sample Code	Description
Polyethylene	
V1-LDPE	Virgin granules transparent white
V2-HDPE	Virgin granules transparent white
LDPE100	Virgin granules transparent white
LDPE650	Virgin granules transparent white
MPE-W3	Virgin tablet white
MPE-W5	Virgin tablet white
MPE-Y	Virgin tablet yellow
MPE-G	Virgin tablet green
HDPE-GQ	Virgin granules transparent white
Polypropilene	
V3-PP-H	Virgin granules transparent white
V4-PP-BC	Virgin granules transparent white
V5-PP-RC	Virgin granules transparent white
PP-GQ	Virgin granules transparent white
PP-R	Regenerated flakes white

A Perkin Spectrum-One™ FT-IR spectrometer was utilised in this study. The optical component of the instrument consisted of a dynamically aligned Michelson

interferometer, a potassium bromide beam splitter and a deuterated triglycine sulfate (DTGS) detector. The instrument is interfaced to Perkin Elmer Spectrum-One™ software. Fourier transform infrared spectra were collected from 7800 to 380 cm⁻¹ at intervals of 4 cm⁻¹. All of the spectral analyses, performed on the different series of plastics samples, were carried out in reflectance conditions. The spectrum of each sample was acquired three times in order to validate the results.

A DeltaNu Advantage 785™ Benchtop Raman Spectrometer equipped with a NuScope™ was utilised to perform PP and PE materials characterisation. The Advantage 785 utilise a 120mW (80mW at sample), 785 nm diode laser, power adjustable, to reduce the fluorescence signature in samples that show strong fluorescence at shorter wavelengths. The investigated spectral range varies between 200-2000 cm⁻¹ with a resolution of 5 cm⁻¹. The NuScope™ allows to perform samples imaging and Raman spectra collection of the acquired domains. Such a device is particularly useful to acquire Raman spectra of specific domains in heterogeneous materials and/or materials where the influence of polluting elements can change the spectral response (e.g. plastics surface affected by surface contamination).

Concerning HSI, two different acquisition systems have been utilised in this study, working in two different wavelength spectral ranges, from 400 to 1000 nm (VIS-NIR range) and from 1000 to 1700 nm (NIR range). The first one consists of a CCD camera, a line scan spectrograph (ImSpector™ V10E, SpecIm™, Finland), a lighting architecture. The spectrograph ImSpector™ V10E operates in the spectral range of 400-1000 nm with a spectral resolution of 2.8 nm. The details of the acquisition architecture are reported in Table 3. The second one is a SpecIm’s NIR spectral camera consisting of an ImSpector N17E imaging spectrograph for the wavelength region 1000-1700 nm and a temperature stabilized InGaAs camera and a

Table 3. Technical Characteristics of the ImSpector™ V10E

Sensor	- 2/3” CCD Array 780x580, - firewire digital output, - pixel resolution: 12 bit.
Spectral range	400 – 1000 nm
Spectral resolution	2.8 nm
Smile	< 1.5 μm
Keoneyst	< 1 μm
Entrance slit	30 μm x 14.2 μm
Image size	6.5 mm x 14.2 mm
Numerical aperture	F/2.4
Illuminant	- anodised Aluminum cylinder, - Barium sulfate internal coating, - d/O illumination and viewing conditions, - adjustable height and distance, - 150 W cooled halogen lamp, - stabilised power source.

lighting architecture (Table 4). Both equipment are mounted on a conveyor belt operated at a variable speed (DV srl, Italy), and are connected to a PC unit with the Spectral Scanner™ v.2.3 [14] acquisition/pre-processing software (Fig. 1).

Table 4. Technical Characteristics of the ImSpector™ N17E

Sensor	- TE-cooled InGaAs photodiode array 640x512 - 14 bit, USB ₂ , LVDS, CameraLink
Spectral range	900 – 1000 nm ± 10nm
Spectral resolution	2.6 nm
Spatial resolution	rms spot radius < 15 μm
Aberrations	Insignificant astigmatism, smile or keystone
Effective slit length	12.8 mm
Numerical aperture	F/2.0
Stray light	< 0.5 % (halogen lamp, 1400 nm notch filter)

6. EXPERIMENTAL RESULTS

The FT-IR spectra of PE and PP samples are reported in (Figs. 2, 3), respectively. The Raman spectra of PE and PP are reported in (Figs. 4, 5), respectively. From the FT-IR and Raman spectral analyses it is evident as the two polyolefins have specific characteristics response in the investigated IR wavelength regions.

Polyethylene is characterized by a simple infrared spectrum as it is made by the polymerization of ethylene ($\text{CH}_2=\text{CH}_2$) and its chemical formula is simply $[\text{CH}_2]_n$ [15]. In fact, the infrared bands of polyethylene are the CH_2 stretching and bending vibrations. As it can be seen from the FT-IR spectra collected in (Fig. 2), the CH_2 asymmetric and symmetric stretches appear at 2917 and 2852 cm^{-1} ,

respectively, the methylene scissoring vibration appears at 1468 cm^{-1} and the rocking vibration appear at 718 cm^{-1} .

Polypropylene is made from the polymerization of propylene ($\text{CH}_2=\text{CH}-\text{CH}_3$) and its structure consists of alternating methylene and methane (C-H) groups, with each repeat unit containing a pendant methyl group [15]. As can be seen from the spectra collected in (Fig. 3), the CH_2 stretching vibrations in the spectrum of PP appear very close to those of PE, at 2921 and 2840 cm^{-1} , respectively. The methyl bands are in the same region, asymmetric and symmetric C-H stretches at 2956 and 2875 cm^{-1} and the umbrella mode at 1377 cm^{-1} . There is not CH_2 rocking band at 720 cm^{-1} because a methane group separates each CH_2 unit from the one next to it. The spectra of PP and PE can be distinguished by the presence of strong methyl group bands in the PP spectrum.

Generally polymers follow the normal trends that strong bands in the Raman spectrum appear relatively weak in the IR spectrum and vice versa. The wavelength field detected by Raman is not representative of the CH stretching region (2700-3000 cm^{-1}) so it cannot be compared to the IR one in that field. The comparison can be done in the fingerprint region (600-1600 cm^{-1}). In the fingerprint region there are C-C stretches, $>\text{CH}_2$ and $-\text{CH}_3$ deformations, and backbone vibrations as well as rocks and wags and twists. In PE (Fig. 4), the backbone vibrational twist occurs near 1300 cm^{-1} and is observed only in the Raman spectrum. The $>\text{C}-\text{C}<$ stretch splits into two bands at 1061 and 1127 cm^{-1} and also appears only in the Raman spectrum. The $>\text{CH}_2$ deformation splits into a triplet in the Raman spectrum, again because of the crystalline phase, and two bands in the IR, with little overlap because of the center of symmetry. In PP (Fig. 5), in addition to the backbone C-C stretches, there are also C-C stretches between the backbone C and the pendant methyl group C that mix in with the backbone stretches.

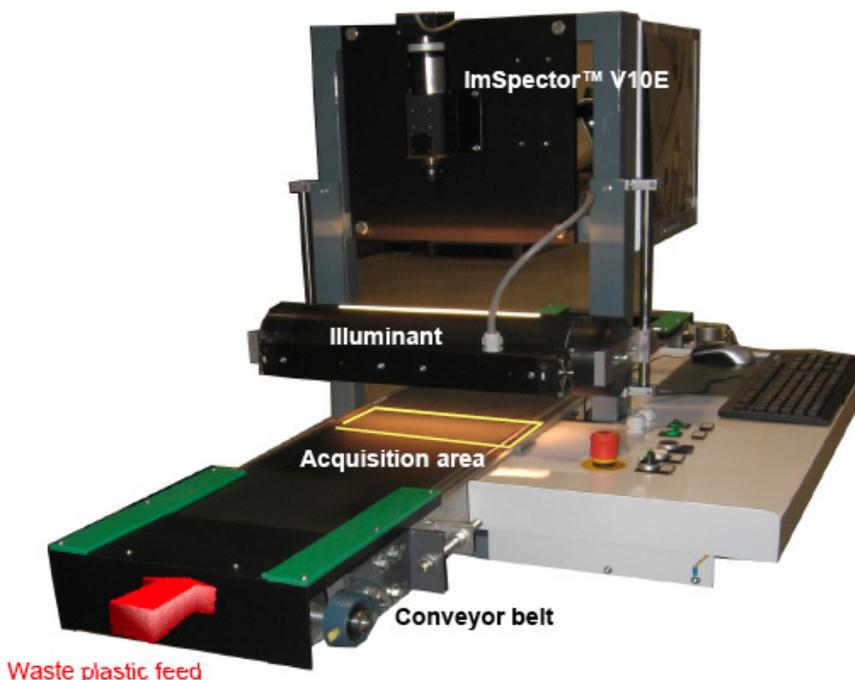


Fig. (1). HyperSpectral Imaging (HSI) based architecture utilized to acquire secondary plastic particles flow streams spectra.

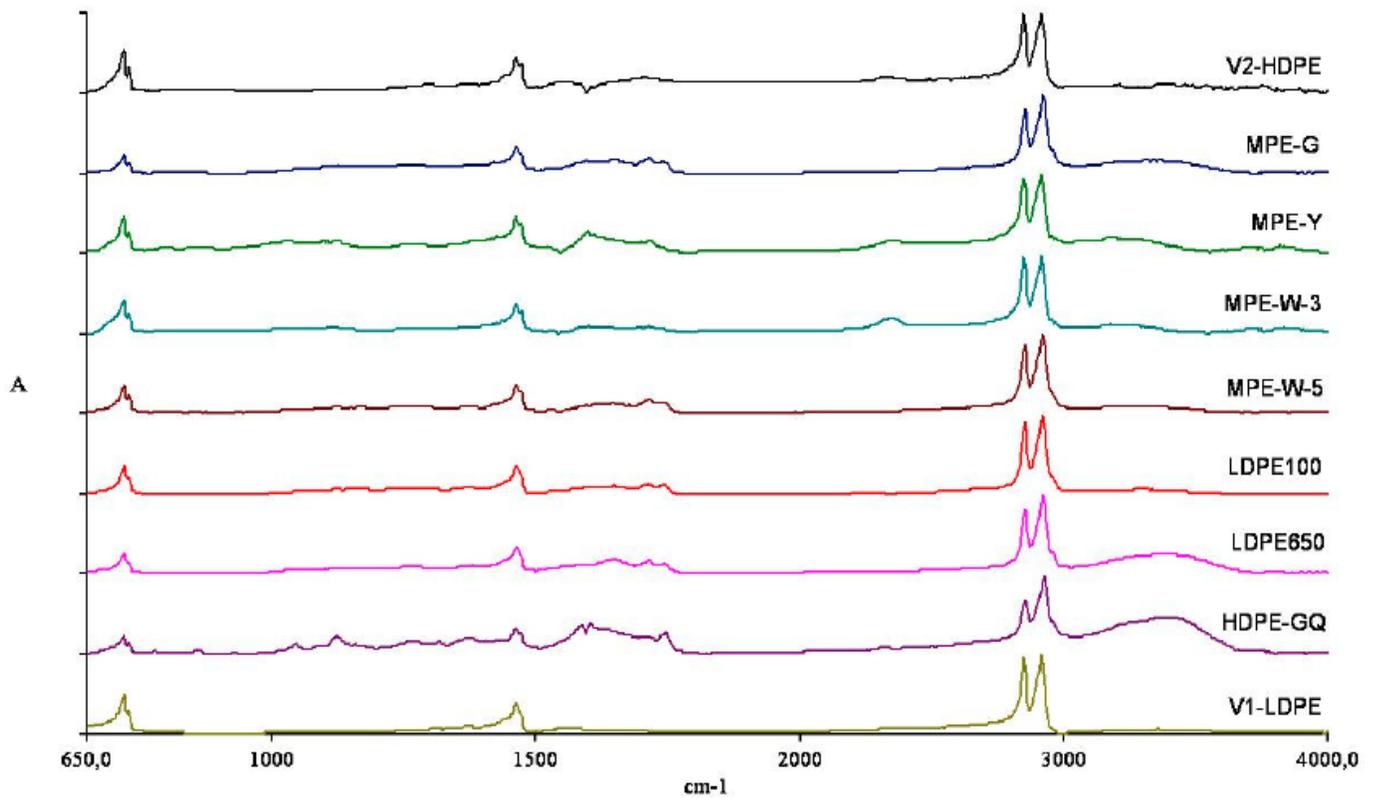


Fig. (2). FT-IR spectra of the polyethylene samples (investigated wavelength range: 650-4000 cm⁻¹).

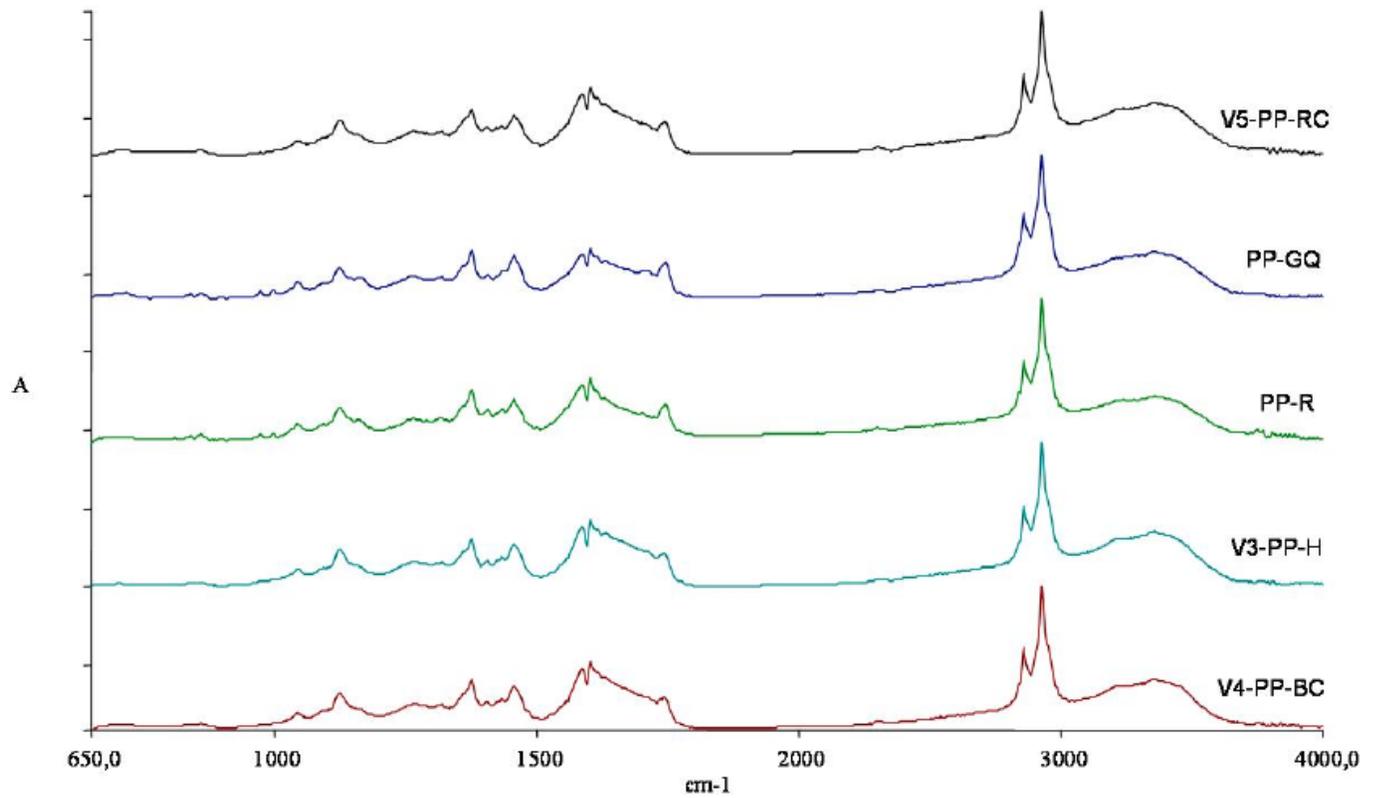


Fig. (3). FT-IR spectra of the polypropylene samples (investigated wavelength range: 650-4000 cm⁻¹).

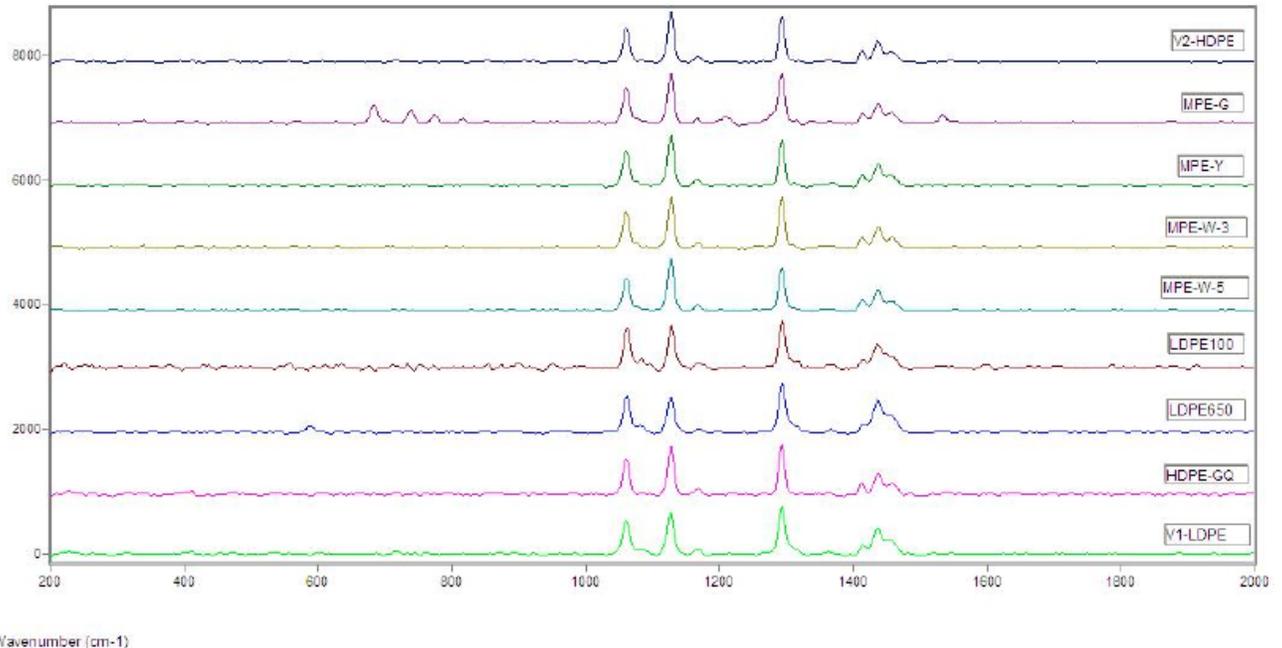


Fig. (4). Raman spectra of the polyethylene samples (investigated wavelength range: 200-2000 cm^{-1}).

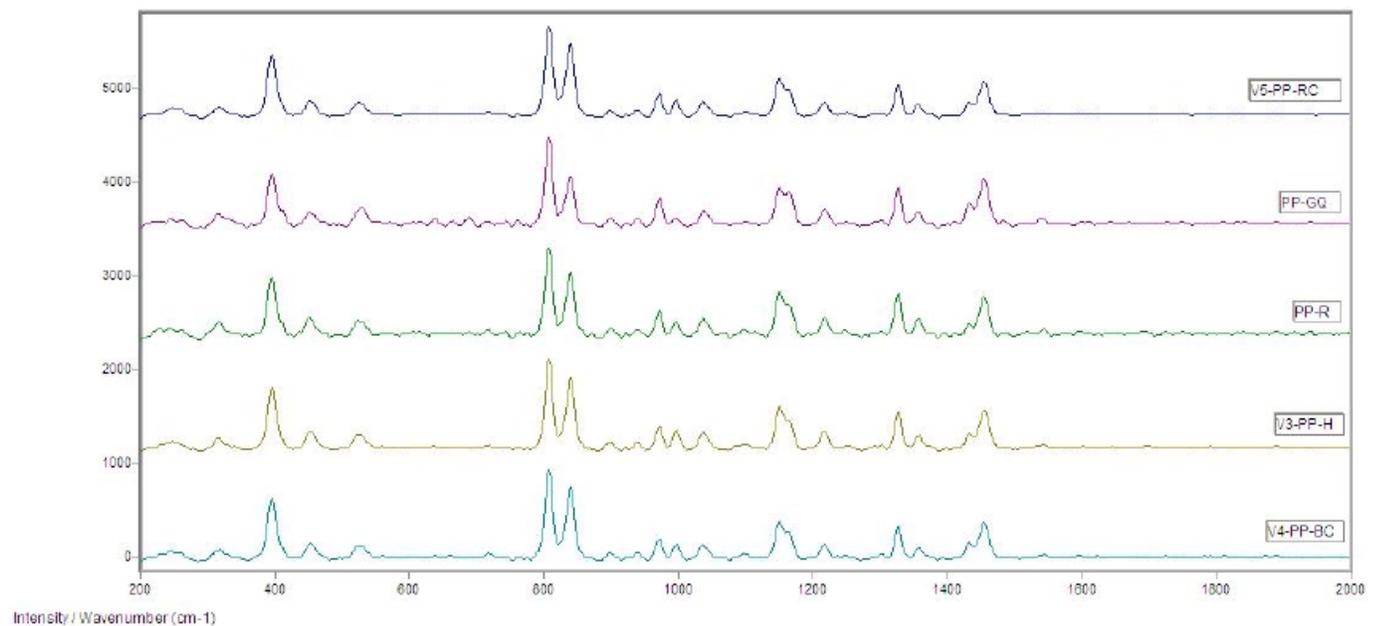


Fig. (5). Raman spectra of the polypropylene samples (investigated wavelength range: 200-2000 cm^{-1}).

What is innovative is the comparison of the spectra obtained by hyperspectral imaging of the two polyolefins in the visible and near infrared region. The reflectance spectra of PE and PP analysed samples are reported in (Figs. 6, 7) for the VIS-NIR wavelength region (400-1000 nm) and in (Figs. 8, 9) for the NIR region (1000-1700 nm). In the visible region, the spectrum is influenced by the color of the analysed sample, but in the NIR region there are processes similar to those occurring in the IR region, corresponding to absorption of overtones (multiple of a vibration) and combinations of vibrations. In particular, the CH overtone regions are around 750 nm, 900-950 nm, 1150-1250 nm, 1350-1450 nm and

1650-1750 nm. As observed in (Figs. 6-9), the spectra shapes of PE and PP are different in all the above mentioned regions due to the different chemical formula and structure of the two polymers and in addition, a difference in the spectra shape is observed also at 1500-1550 nm.

Based on the analysis of HSI spectra, it is evident the possibility to define specific parameters useful for recognition of the two polyolefins, as for example the slope of the spectrum in a selected wavelength range or a band ratio among two different wavelengths. It is important to outline that the best and most precise recognition logic

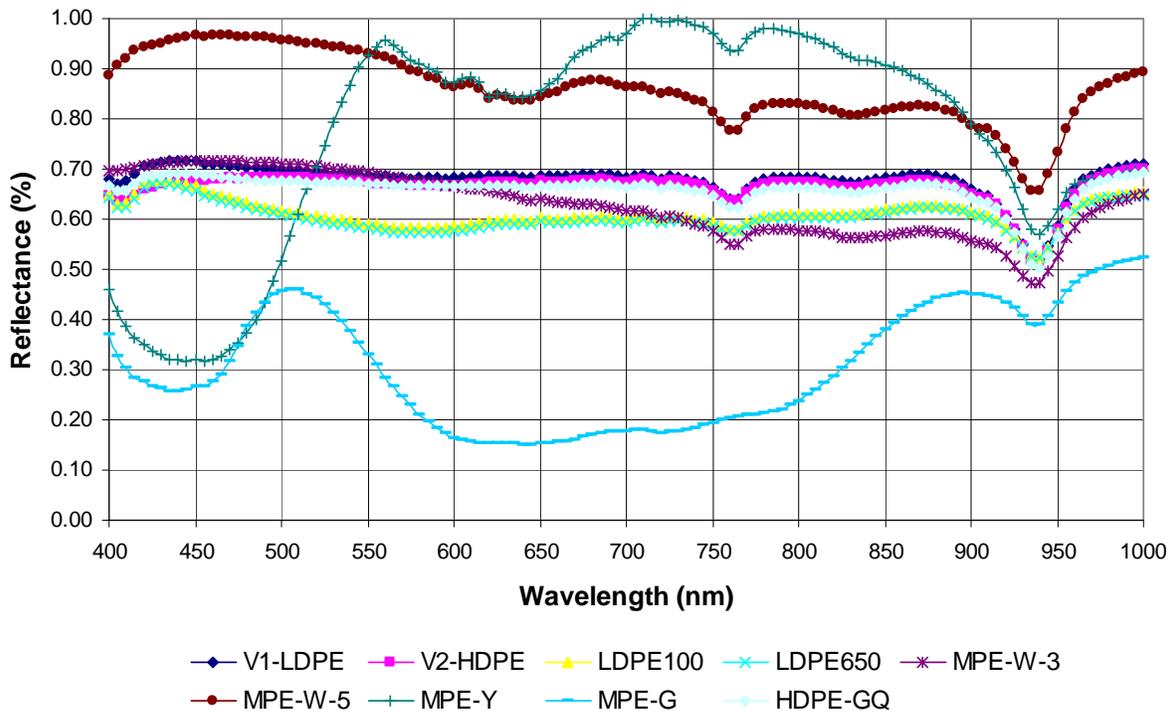


Fig. (6). HSI reflectance spectra of the polyethylene samples (investigated wavelength range: 400-1000 nm).

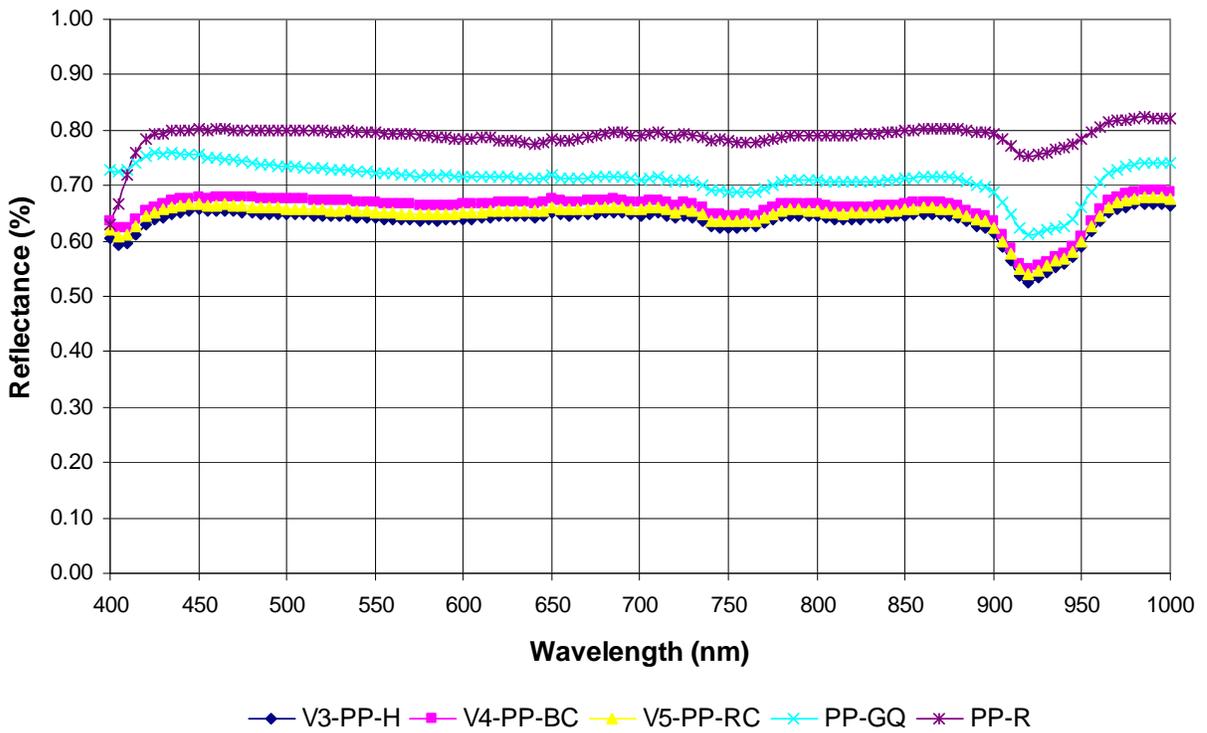


Fig. (7). HSI reflectance spectra of the polypropylene samples (investigated wavelength range: 400-1000 nm).

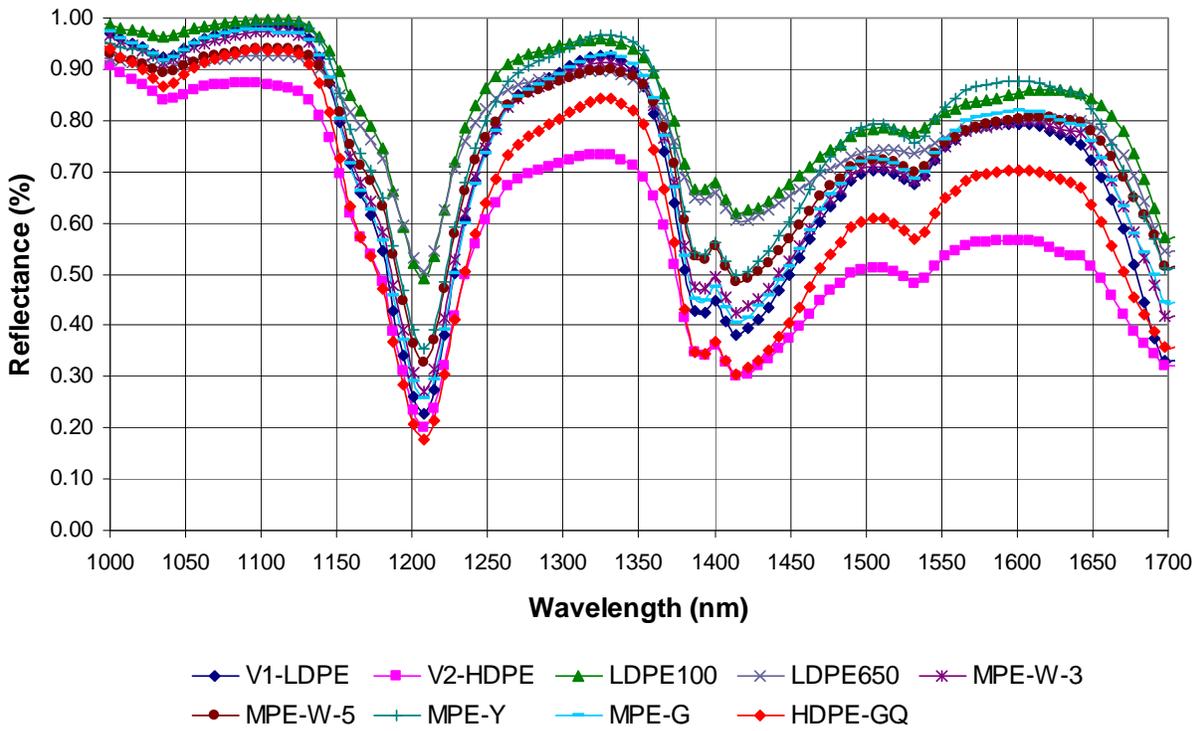


Fig. (8). HSI reflectance spectra of the polyethylene samples (investigated wavelength range: 1000-1700 nm).

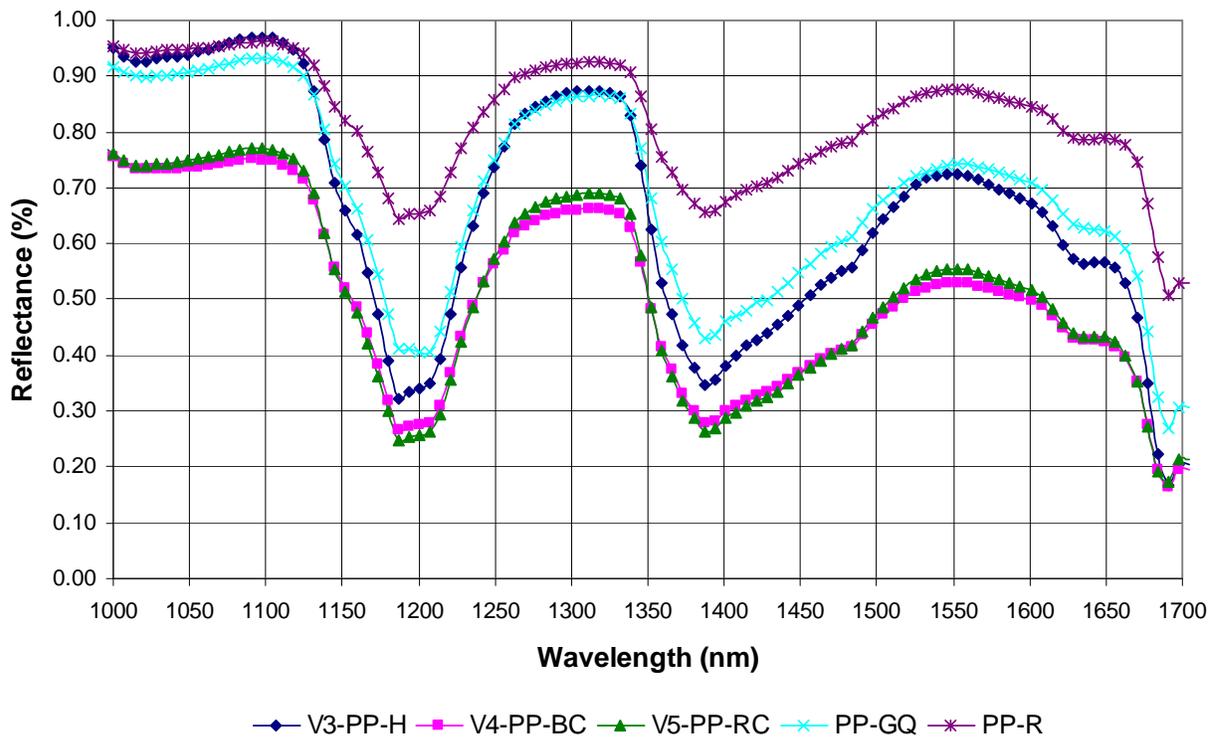


Fig. (9). HSI reflectance spectra of the polypropylene samples (investigated wavelength range: 1000-1700 nm).

should be based on more sophisticated and complex statistical analyses, such as Principal Component Analysis (PCA), Partial Least Square (PLS), Neural Network (NN), etc., that usually require long computation time. Considering that in most industrial applications the fast response of the detecting/sorting device is one of the main constraints, as for example when particles are moving on a conveyor belt and they are sorted on-line, the adoption of simplified logics, obviously working properly, as that proposed in this study, is preferred. Such simplified logics, based on the selection of a limited number of wavelengths, not only decrease computation time, but also decrease the costs of the device.

7. CONCLUSIONS

The possibility to apply an HSI approach to identify PE and PP was investigated. Such an approach was developed in the perspective to utilise the previous mentioned procedure to perform an on-line sorting of plastic waste streams in order to recover polyolefins. A systematic preliminary characterisation of different PE and PP materials of different colors was carried out adopting "classic" and well established analytical techniques as FT-IR and Raman spectroscopy. The results have been compared with those obtained by the innovative proposed HSI approach in the perspective to utilise such a techniques to develop PE and PP micro-sorting strategies. Results showed as the HSI allows correctly identify the different polyolefins samples.

Selecting the right parameter representing the different spectral signature, it is thus possible to recognize the two polyolefin typologies, PE and PP. To define an efficient fast and reliable sorting strategy, finalized to the identification of optimal system requirements, the parameters related to specific wavelength ratios seem to be the best matching the goal also for the intrinsic processing speed of the procedure, simplifying the sorting architecture, reducing this way equipment costs and allowing high production rates.

The proposed approach can be utilized:

- to develop innovative on-line sorting logics, that is the identification of PE and PP particles inside a flow stream of assorted material to recycle for their further separation by an air-jet system,
- to implement process control strategies, adopting suitable detection strategies and analytical tools, able to perform a comparison of plastic particulate materials before and after a specific separation stage (i.e. heavy media, flotation, electronic, magnetic, eddy current, etc.), and eventually modify the working parameters of the process itself,
- to define quality control actions, defining the characteristics of the final produced material, that is presence of impurities that can prejudice both

chemical compatibility and/or processing temperature.

In an industrial-quality control perspective applied to waste streams characterisation the systematic application of HSI can open new interesting scenarios especially for waste plastic products difficult to qualify/sort with actually applied strategies.

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