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Elaboration and Characterization of Traced Polypropylene with Rare Earth Oxides for Automatic Identification and Sorting of End-of-Life Plastics

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Abstract The rare earth oxides can be used as tracers for the identification of polymer materials. This study focused on the detection of these particles and their effects on the mechanical and thermal properties of polypropylene (PP). A new method was carried out to increase the sorting selectivity of PP during end of life recycling process and to improve the efficiency of sorting and its high speed identification. The tests were realized in a test system device which allows the collection of static measurements of the samples spectrum through the use of energy dispersive X-ray fluorescence technology. Five of the seven tracers tested are clearly visible and distinguishable from the background sample by their $K_{\alpha 1}$ energy line at concentration levels of 0.1 and 0.145 wt%. For the two remaining tracers, their $K_{\alpha 1}$ energy lines come out at the same domain of energy as the source. Dispersion of rare earth oxides at 0.1 and 1 wt% do not have a significant impact on the crystallization and melting temperature as well as on the temperature of maximum decomposition rate. The addition of 1 wt% of rare earth oxides leads to a slight increase of the flexural modulus, whereas the addition of 0.1 and 1 wt% causes a decrease of the elongation at break. SEM images show a homogenous dispersion of tracers in the PP matrix.

Introduction

Plastics have an impact on the environment, society and economic dimensions. The consumption of plastics materials reached an overall of 53.5 million tons in 2004 according to the Association of Plastics Manufactures in Western Europe. Of the plastics consumed, the breakdown by sector indicates that 37% of the plastic were used for packaging, 20% for construction, and 7.5% for the electrical/electronics industry with a further 7.5% being used by the automotive industry [1, 2].

Conventional plastics manufactured from these petroleum polymers generally degrade very slowly in the environment and the recycling process is very difficult since they are incompatible with each other. Currently, the energetic recovery of plastic wastes is achieved through easy options as incineration, which may cause the emission of harmful gases together with generation of toxic fly and bottom ash that contain lead and cadmium [3–5]. Moreover, energy recovery is a consumptive recycling process, turning the recycled material into energy rather than usable material, and thus does not conform to the reuse-ration required by the European legislations and directives [6].

The automotive and electrical industries are currently the worst performers due to the complexity of the waste materials that these sectors produce. In 2004, a study

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showed that in France, 82% of plastic wastes coming from ELV (End-of-life Vehicles) and WEEE (Waste of Electric/Electronic Equipments) were sent to landfill [7]. To resolve this problem, the European Commission has recently introduced very strict regulations [8, 9]. For example, in the case of automotive sector, a ratio of 5% of ELV residues landfill deposal is required in the framework of developing solutions in order to reduce the impact of end of life products.

Therefore, it is necessary to improve technologies such as the sorting of polymer materials so as to make their recycling profitable. For an economically efficient recycling of polymer materials, waste plastics need to be sorted cheaply and automatically into individual types and grades [10].

Techniques based on optical spectroscopy, such as infrared reflection/absorption [11–13] have reached their limits. They are unsuitable for dark objects such as those containing carbon black that absorb and scatter at NIR frequencies, and they can neither identify different grades of the same polymers nor be used if the surface of the plastic wastes is wet, painted or dirty.

The technique of high resolution imaging using X-rays is limited to the separation of PVC from PET [14] and the elimination of PVC and brominated aromatic compounds contained in the electronic wastes and substituted combustibles.

In 1992, Ahmad et al. [15, 16] developed a new concept of identification of plastics by incorporating fluorescent tracers into the polymers and giving them a fluorescent signature in Ultra Violet spectroscopy. This research concluded that the speed and purity of sorting were limited by the mechanical singulation inadequacy of the conveyor system at high speed and that the pigments found in plastics reduced the fluorescence yield, whereas in the case of black pigments, the reduction was too drastic to permit identification. Aside from these limitations, Ultra Violet spectroscopy is a surface detection method and this implies a "clean" surface for tracer identification.

The challenge of overcoming the inefficiency of existing sorting technologies associated with the need for identifying black plastic wastes coming from the ELV and WEEE, has led to the development of new methods of identification of polymeric materials.

The principal objectives of this work are to prove the technical feasibility of detection of tracers (rare earth oxides) added to polypropylene through the use of XRF (X-ray fluorescence) spectrometry and to study their effect as fillers, on the thermal and mechanical properties of traced materials. In previous work [17], the authors have already reported some parameters which can influence the detection of tracers.

XRF spectrometry is a volume, non-destructive elemental analysis. Compared to Ultra Violet fluorescence the detection process is not affected by black pigments, and a "clean" surface is not required due to a volume detection of around 1 mm depth. Nevertheless, as XRF is a spectroscopic method enabling elemental analysis of material, therefore the number of tracers is limited to the elements of Mendeleyev's Periodic Table.

The choice of rare earth oxides as tracers was achieved by eliminating from the Mendeleyev's Periodic Table, the toxic and radioactive elements, in addition to elements contained in polymer additives, low atomic number elements; which do not give an intense signal and elements which do not have important reserves.

The choice of polypropylene, one of the world's major plastics, was justified by its large use in the fields of automotive and electric/electronic industries. Supposing that another polymer matrix was studied, the detection results would have been the same as that of the PP matrix, since polymers are generally composed of elements, such as hydrogen, carbon, nitrogen and sulphur, which have a low atomic number and hence will not hinder tracer identification. Regarding the thermal and mechanical properties, the tracer concentration should be included within a range [0.01–0.1 wt%], in order to avoid their effect on the properties of the polymer matrix.
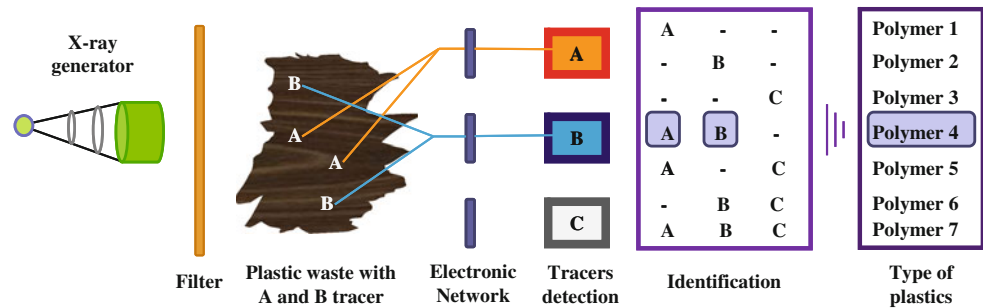
Tracers Identification

It turns out that the effectiveness of sorting and in particular the speed of identification of plastic wastes can be improved by the use of a tracer system giving a unique signature to each type and grade of polymer. In the detection system shown in Fig. 1, the excitation of the tracers is carried out through the use of an X-ray source and their detection is achieved by X-ray fluorescence spectrometry. This work of identification technology was first proposed by Ahmad et al. [18, 19], who used fluorescent tracers emitting in Ultra Violet spectrometry.

The identification system is based on the dispersion of very small quantities of one or more substances-tracers-emitting X-ray fluorescence into the plastics requiring identification. The concentration of the tracers must be within a range of [0.01–0.1 wt%], in order not to influence the properties of the polymer matrix.

Due to the great diversity of the nature of plastics, including the types of polymers, as well as the grades, the additives and colorants, it is not practical to have a tracer for each potential variant. To overcome this constraint, tracers can be used in a matrix, such that each combination corresponds to a type, grade or additive. For example,

Fig. 1 Principle of tracers' identification by binary code

theoretically, by using only 3 tracers, it is possible to identify 7 ($2^3 − 1$) variations of different plastics.

The identification is carried out by exciting the plastics using an X-ray source. This radiation is absorbed by the tracers, which are excited to higher atomic energy levels. Each tracer emits a unique radiation of X-ray fluorescence, which depends on the atomic number of the element. The detection system, coupled with a data processing system, detects the emitted radiation and identifies the signature of the tracer, and thus the nature of the polymer matrix.

Experimental Part

Materials

ISPLEN PP 050 G1E is a medium melt flow rate polypropylene homopolymer particularly formulated and adapted for injection moulding and extrusion applications. It is intended for applications that require good impact resistance balanced with high stiffness. The original pellets have a melt mass-flow rate of 5.8 g/10 min (2.16 kg at 230°C) and a density of 0.905 g/cm^3.

The rare earth oxides used as tracers are described in Table 1. The rare earth oxides were chosen as tracers because they satisfy the required specifications [21–23]. They are compatible, not abrasive and stable in the environment of evolution. They are also non toxic [24, 25]

during their application and use. Regarding the detection method, they have a high atomic number, facilitating their detection in X-ray fluorescence.

The prices given by AMPERE for a purity of 99.9% for one tonne of rare earth oxides of Y_2O_3, CeO_2, Nd_2O_3, Gd_2O_3 and Er_2O_3, and for 10 kg of Dy_2O_3 and Yb_2O_3 are shown in Table 1. As it can be seen in the table, for 1 g of tracer per 1 kg of plastic, the prices vary from 0.006€, in the case of cerium oxide to 0.34€, in the case of dysprosium oxide. Prices of rare earth oxides will also depend on the "Supply and Demand" economic model and may decrease in the case of Dy_2O_3 and Yb_2O_3, so as to equalize the quantity demanded by consumers, and the quantity supplied by producers, resulting in an economic equilibrium of price and quantity.
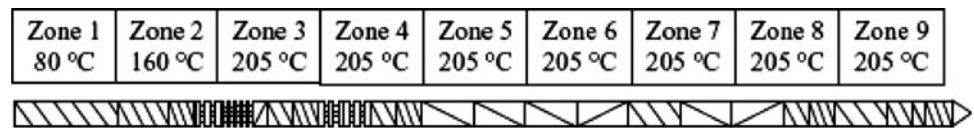
Dispersion of Tracers

All traced polypropylene samples were prepared under identical mixing and moulding conditions. Several samples of polypropylene containing the rare earth oxides in different concentrations were prepared for analysis (Table 2), using a twin screw extruder CLEXTRAL BC21 machine with a screw of L/D = 90 and D = 25 mm. The extrusion temperature and screw speed were 205°C and 120 rpm respectively and the residence time 15 min. The screw and temperature profiles used in this study are supplied in Fig. 2.

Table 1 Materials specifications

Materials	Chemical name	Supplier	Mean particle diameter (μm)	Density (g/cm)	Toxicity (LD 50)	Prices in € for 1 g	Mass concentration in lithosphere [20]
PP	Polypropylene	REPSOL	2000	0.905	–	–	H → 1.5×10^{-3}, C → 10^{-3}
Y_2O_3	Yttrium oxide	RHODIA	2.250	5	>5000 mg/kg	0.012	50×10^{-6}
CeO_2	Cerium oxide	RHODIA	2.250	7.3	>5000 mg/kg	0.006	46×10^{-6}
Nd_2O_3	Neodymium oxide	AMPERE	3.500	7.24	>1000 mg/kg	0.022	24×10^{-6}
Gd_2O_3	Gadolinium oxide	RHODIA	1.850	7.4	>1000 mg/kg	0.075	6×10^{-6}
Dy_2O_3	Dysprosium oxide	RHODIA	2.250	7.8	>1000 mg/kg	0.340	0.5×10^{-6}
Er_2O_3	Erbium oxide	AMPERE	8.200	8.6	>1000 mg/kg	0.022	2×10^{-6}
Yb_2O_3	Ytterbium oxide	AMPERE	1.000	9.2	>1000 mg/kg	0.250	3×10^{-6}

Table 2 Characteristics of traced PP samples

CodePP/tracer_wt%	Tracer	Mass composition of each tracer (wt%)	Volume composition of each tracer (vol.%)
PP_reference	PP-reference	0	0
PP/Nd$_2$O$_3$_0.1	Nd$_2$O$_3$	0.1	0.140
PP/Nd$_2$O$_3$_1	Nd$_2$O$_3$	1	1.402
PP/Gd$_2$O$_3$_0.1	Gd$_2$O$_3$	0.1	0.119
PP/Gd$_2$O$_3$_1	Gd$_2$O$_3$	1	1.191
PP/all_0.025	Y$_2$O$_3$, CeO$_2$, Nd$_2$O$_3$	0.025	0.029
PP/all_0.1	Gd$_2$O$_3$, Dy$_2$O$_3$	0.1	0.113
PP/all_0.145	Er$_2$O$_3$, Yb$_2$O$_3$	0.145	0.163

Fig. 2 Screw and temperature profiles for the extrusion processing

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9
80 °C	160 °C	205 °C	205 °C	205 °C	205 °C	205 °C	205 °C	205 °C

The pellets obtained from extrusion were then injected in a Battenfeld Unilog B2/350 Plus injection moulding machine. A general purpose screw was used in the barrel, which was kept at 220°C. Specimens of diameter 6 cm and thick 2 mm were injected, for the X-ray fluorescence analysis.

Characterisation of Tracers' Dispersion

The dispersion of tracers in the PP matrix was investigated by scanning electron microscopy (SEM) using a Hitachi S3500 N model. The specimens were prepared by injection moulding with a press Battenfeld Unilog B2/350 Plus and fractured in liquid nitrogen and sputter-coated with gold before being examined with the microscope at an accelerating voltage of 30 kV.

Thermal Properties

Thermal properties of blends were measured by differential scanning calorimetry using DSC Q10 of TA Instruments. The samples were cut from probes and placed in aluminium pans and then heated in an argon atmosphere from room temperature to 210°C under a controlled heating rate of 10°C/min. Cooling of the samples was performed from 210 to 0°C with a cooling rate of 10°C/min after holding the samples at 210°C for 5 min. The sample mass was typically between 5 to 10 mg. The degree of crystallisation, χ_C, was calculated considering a melting enthalpy of 209 J/g for a 100% crystalline polypropylene.

Thermal stability of specimens was characterized by using a thermogravimetric analyzer (Q500 Thermogravimetric Analyzer, TA Instruments). Measurements were conducted under an argon flow rate of 90 mL/min at heating rate of 20°C/min. The scanning temperature ranged from 25 to 500°C. Similar to the DSC characterizations, small samples of 10–15 mg were cut from probes for measurement. The temperature of maximum decomposition rate (T_{max}) was calculated for each traced PP sample.

Mechanical Characterisation

Tensile test specimens were prepared according to ISO 527-1:1993. Tensile mechanical tests were made with an Instron Machine Model 4469 at ambient temperature. Young's modulus was measured at 1 mm/min cross-head speed with a strain of between 0.05 and 0.3%. Yield stress and elongation at break were measured at cross-head speed of 250 mm/min and evaluated from stress–strain curves on an average of at least six specimens.

X-ray Fluorescence Device

The X-ray fluorescence device, developed by NRT, is a test system which allows taking static measurements of the samples spectrum. A schematic of a typical EDXRF (energy dispersive X-ray fluorescence) spectrometer is shown in Fig. 3. The X-ray radiation from the X-ray source passes through a hole onto the sample and then travels to the detector.

The signal from the detector is then processed electronically and sent to the computer, which also controls the X-ray source. The XRF spectra can then be analyzed and used for the separation of the samples containing the tracers.

This EDXRF technique [26] is a two-step process that begins with the removal of an inner shell electron of an atom. The resulting vacancy is filled by an outer shell
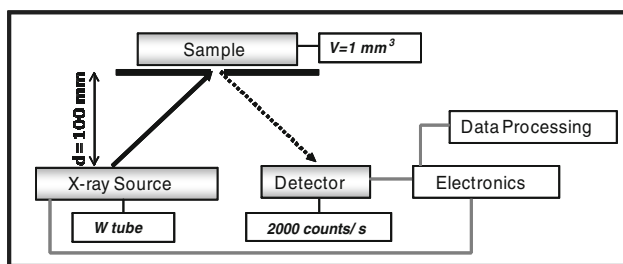
Fig. 3 Schematic of the EDXRF device

electron. The second step is the transition from the outer shell electron orbital to an inner shell electron orbital. The transition is accompanied by the emission of X-ray photon. The fluorescent photon is characteristic of the element and is equal to the difference in energy between the two electron energy levels. Because the energy difference is always the same for given energy levels, the element can be identified by measuring the energy of the emitted photon.

The emission process is similar to other fluorescent measurement techniques, but it is restricted to the X-ray region of the electromagnetic spectrum that ranges from 4 to over 80 keV. The photon energies detected are designed as K, L, or M X-rays, depending on the energy level being filled. For example, $GdK_{\beta 1}$ represents, for the gadolinium element, the transition corresponding to the passage of M to K level and 1, the relative intensity of the transition in the series (1, more intense than 2). There are as many possible X-ray lines as there are inner shell electrons. However, the most analytically useful and most intense X-ray lines are the K shell electrons. Although, the multitude of emitted X-ray lines could result in complex spectra, the relative low intensities of the lines below the L level allow obtaining a clear spectrum with minimal interference.

The volume of the analysed sample was 1 mm^3. The distance between the sample and the source was 10 cm and the angle 45°. The detection time was 1 min and the detector could make 2,000 counts/s. The X-ray source used was a tungsten tube.

Results and Discussions

Detection of Tracers and Concentration Effect

The objective of these tests was to prove the detection of the 7 selected tracers in the PP matrix. Table 3 shows the expected energies of the elements composing the tracers. The detection of tracers is separated in two domains. The first one, between 7 and 20 keV ($L_{\alpha 1}$, $L_{\beta 1}$ of ytterbium and $K_{\alpha 1}$, $K_{\beta 1}$ of yttrium) and the second between 34 and 60 keV ($K_{\alpha 1}$, $K_{\beta 1}$ of cerium to ytterbium). The tested samples contained all the tracers in three different

concentrations (PP/all_0.025, PP/all_0.1 and PP/all_0.145). The exposure time for the four samples was 1 min. The obtained spectrum is shown in Fig. 4.

As shown in the spectrum, five of the tracers (Y_2O_3, CeO_2, Nd_2O_3, Gd_2O_3 and Dy_2O_3), at concentration levels of 0.1 and 0.145 wt%, are clearly visible and distinguishable from the "background" sample by their $K_{\alpha 1}$ energy line.

For the same five tracers at 0.025 wt%, the fluorescent peak is not sufficiently different from the background in order to make a positive identification.

Concerning the detection of Er_2O_3 and Yb_2O_3, their $K_{\alpha 1}$ energy lines (49.12 and 52.38 keV respectively) are emitted in the same domain of energy (49–53 keV) as the tungsten source ($WK_{\alpha 1}$: 59.31 keV), which is rescheduled at about 8–9 keV.

Regarding the detection of the $L_{\alpha 1}$ and $L_{\beta 1}$ energy lines of CeO_2, Nd_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3 and Yb_2O_3, a large fluorescent peak appears in the range [5–9 keV] corresponding to these energies. Consequently, it is difficult to distinguish the $L_{\alpha 1}$ and $L_{\beta 1}$ energy lines of these elements.

Moreover, the detection of the $L_{\alpha 1}$ and $L_{\beta 1}$ energy lines present three additional difficulties:

– They have significantly less fluorescent yield than the K energy lines.
– They are much closer in energy to other elements which might be present (example cerium vs. titanium) and thus require a combination of longer exposure times and more sensitive detectors.
– The lower energy of L X-rays are more easily absorbed by air, plastic dust coverings, thin metal foils, that are present in the construction of an "industrial" sorting environment.
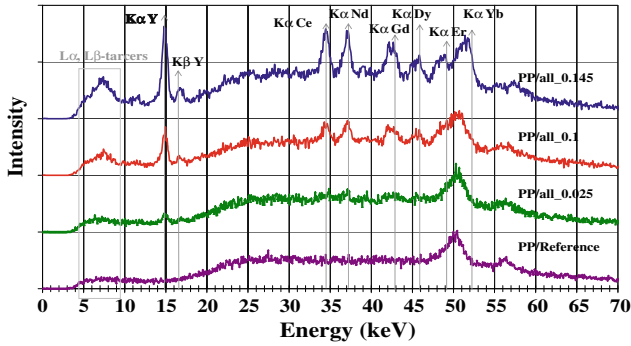
Thermal Properties

The minerals used as fillers in polypropylene are principally talc and calcium carbonate. However, little attention has been paid to rare earth compounds used as fillers in polymers. As rare earth minerals are abundant in China, studies investigating PP composites containing rare earth compounds were published by Chinese scientists.

Liu et al. [27, 28] have studied the effect of a large number of rare earth oxides on isothermal crystallization and melting behaviour with differential scanning calorimetry. They found that a series of rare earth oxides in a fine powder form may act as a nucleator and influence the growth rate of the spherulite and the mechanical properties of polypropylene.

Other studies of Xiaomin et al. [29] have shown that the addition of Y_2O_3 has some effect on the viscosity of the system. Crystallization characteristics have indicated that

Table 3 X-ray fluorescent energy values of tracers' elements [19]

Energy lines (keV)	Y_2O_3 Y	CeO_2 Ce	Nd_2O_3 Nd	Gd_2O_3 Gd	Dy_2O_3 Dy	Er_2O_3 Er	Yb_2O_3 Yb	Source W
$K_{\alpha 1}$	14.96	34.71	37.36	42.99	45.99	49.12	52.38	59.31
$K_{\beta 1}$	16.74	39.26	42.27	48.72	52.18	55.69	59.35	67.23
$L_{\alpha 1}$	1.92	4.84	5.23	6.06	6.49	6.95	7.41	8.40
$L_{\beta 1}$	1.99	5.26	5.72	6.71	7.25	7.81	8.40	9.67

Fig. 4 Comparison of XRF spectra of PP/reference, PP/all_0.025, PP/all_0.1 and PP/all_0.145

the filler acts as a nucleating agent, increasing crystallization degree of the investigated polymer, and changing β crystal form content.

Along this work, the thermal properties of PP composites containing rare earth oxides were studied. The values of melting and crystallization enthalpies and temperatures, the maximum decomposition rate temperature and the crystallization degree of PP containing Gd_2O_3, Nd_2O_3 and all the tracers are listed in Table 4. Figure 5 includes the DSC data and the way in which enthalpies and temperatures where calculated.

The addition of tracers within the concentration range of [0.1–1 wt%] to the PP matrix does not seem to influence the melting and crystallization enthalpies and temperatures as well as the crystallization degree. Even if an increase of

the crystallization degree at 1 wt% was expected, the size of neodymium and gadolinium oxide particles is not small enough so as to act as a nucleator agent. Regarding the thermal stability, the addition of rare earth oxides improves slightly the degradation level of the PP matrix as the T_{max} increases with tracer content.

The fact that tracers at 0.1% do not influence the thermal properties of the PP matrix means that it is not necessary to take further precautions for plastic processing of polypropylene, since the melting and crystallization temperature and enthalpies remain unchanged.
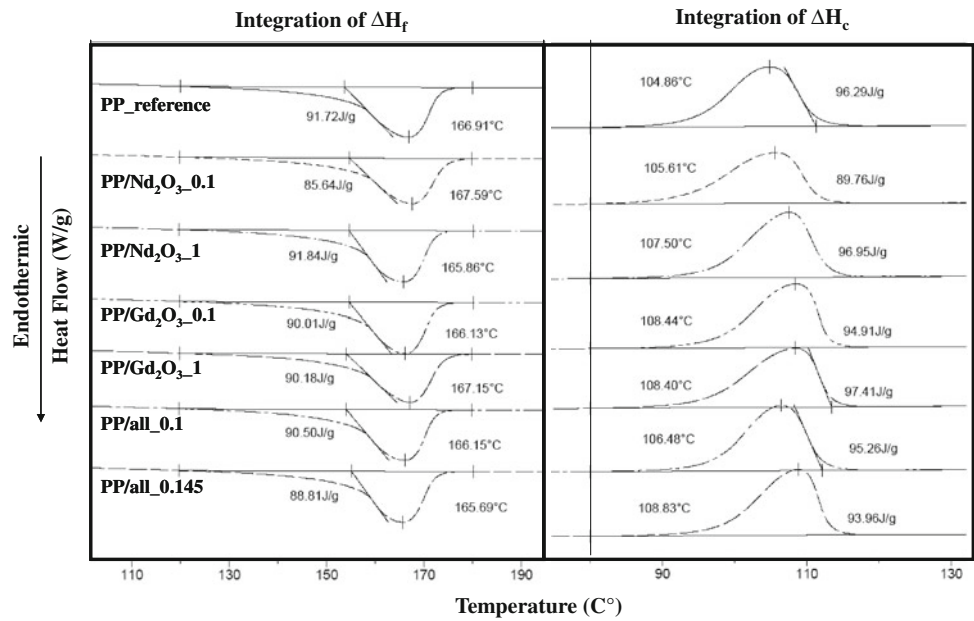
Characterisation of the Dispersion of Tracers

An important parameter of our study is the dispersion of tracers in the PP matrix. The homogenous dispersion of tracers will allow a good detection by X-ray fluorescence spectrometry for a given surface. It is also noted that the better they are dispersed in the PP matrix, the lower will be the modifications on the mechanical properties.

The morphology of the compounds up to a concentration of 1% of gadolinium oxide and neodymium oxide is shown in Fig. 6. The morphology consists of finely dispersed particles in the PP matrix. In both samples, for a scanning surface of 0.15 mm², no aggregates were observed. This is probably because they are broken up to primary particles during the extrusion process. The SEM images were analysed by MATLAB by applying image processing. The obtained particle size was approximately 1 μm for both Gd_2O_3 and Nd_2O_3.

Table 4 Thermal properties and crystallization degree of traced PP samples obtained by DSC and ATG

Sample	ΔH_f (J/g$_{PP}$)	T_f (°C)	ΔH_c (J/g$_{PP}$)	T_c (°C)	χ_c (%)	T_{max} (°C)
PP_reference	92 ± 3	166.9 ± 0.5	96 ± 3	104.9 ± 0.5	44 ± 1	471.7 ± 0.5
PP/Nd_2O_3_0.1	86 ± 3	167.6 ± 0.5	90 ± 3	105.6 ± 0.5	41 ± 1	473.6 ± 0.5
PP/Nd_2O_3_1	92 ± 3	165.9 ± 0.5	97 ± 3	107.5 ± 0.5	44 ± 1	473.9 ± 0.5
PP/Gd_2O_3_0.1	90 ± 3	166.1 ± 0.5	95 ± 3	108.5 ± 0.5	43 ± 1	475.0 ± 0.5
PP/Gd_2O_3_1	90 ± 3	167.2 ± 0.5	97 ± 3	108.4 ± 0.5	43 ± 1	476.2 ± 0.5
PP/all_0.1	91 ± 3	166.2 ± 0.5	95 ± 3	106.5 ± 0.5	43 ± 1	475.2 ± 0.5
PP/all_0.145	89 ± 3	165.7 ± 0.5	94 ± 3	108.8 ± 0.5	43 ± 1	475.8 ± 0.5

Fig. 5 Melting and crystallization peaks of traced PP samples after the 2nd heating run

Integration of ΔH_f

Integration of ΔH_c

Endothermic Heat Flow (W/g)

PP_reference	91.72J/g	166.91°C	104.86°C	96.29J/g
PP/Nd$_2$O$_3$_0.1	85.64J/g	167.59°C	105.61°C	89.76J/g
PP/Nd$_2$O$_3$_1	91.84J/g	165.86°C	107.50°C	96.95J/g
PP/Gd$_2$O$_3$_0.1	90.01J/g	166.13°C	108.44°C	94.91J/g
PP/Gd$_2$O$_3$_1	90.18J/g	167.15°C	108.40°C	97.41J/g
PP/all_0.1	90.50J/g	166.15°C	106.48°C	95.26J/g
PP/all_0.145	88.81J/g	165.69°C	108.83°C	93.96J/g

Temperature (C°)

Fig. 6 a SEM images of fractured specimens of gadolinium oxide dispersed in the PP matrix at 1% **b** SEM images of fractured specimens of neodymium oxide dispersed in the PP matrix at 1%
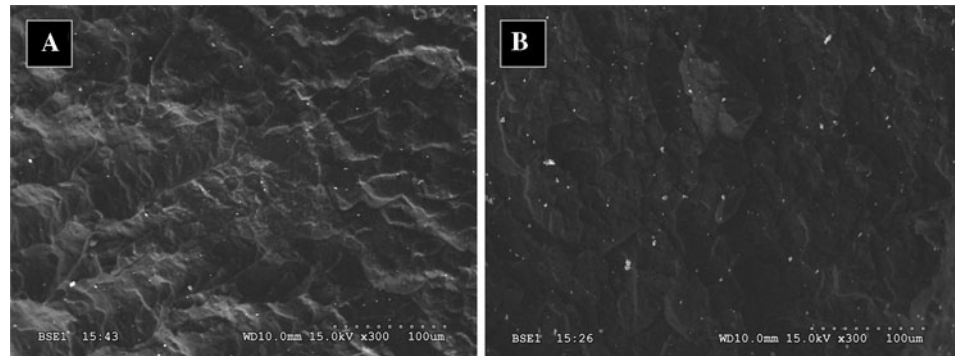
Table 5 Image processing results obtained with MATLAB

Sample	d_{th_cubic} (μm)	$d_{th\_hexagonal}$ (μm)	$d_{calculated}$ (μm)	Mean particle size (μm)
PP/Nd$_2$O$_3$_1	19.8	14.2	17.3	1.06
PP/Gd$_2$O$_3$_1	17.7	12.7	14.5	0.86

The dispersion of rare earth oxides particles was estimated by comparing the distance ($d_{calculated}$) of the first ten neighbouring spheres calculated for the SEM data and the theoretical distance for a cubic (d_{th_cubic}) or a hexagonal ($d_{th\_hexagonal}$) close packing arrangement (Table 5). In the case of neodymium oxide the arrangement is more near to the cubic close packing arrangement whereas the gadolinium oxide is arranged into a hexagonal close packing. Both SEM images and data obtained by image processing show a homogenous dispersion of gadolinium and neodymium oxide into the PP matrix.

Mechanical Characterisation

The inorganic fillers can change the characteristics of a polymer in two ways: Primarily, the properties of particles themselves such as size, shape and modulus can have a profound effect, especially on mechanical properties. Secondarily, the particles may cause a change in the micromorphology of the polymer, which may then give rise to differences in the observed bulk properties. In order to study the influence of rare earth oxides on the mechanical properties of the PP matrix, the tensile properties of traced PP are shown in Table 6.

Table 6 Tensile mechanical properties of traced PP samples at room temperature

Sample	Young's modulus E (MPa)	Yield stress σ_y (MPa)	Elongation at break ε_b (%)
PP_reference	665 ± 28.8	50.5 ± 0.5	99.7 ± 5.4
PP/Nd$_2$O$_3$_0.1	670 ± 17.4	48.8 ± 0.4	78.6 ± 6.6
PP/Nd$_2$O$_3$_1	685 ± 11.6	49.0 ± 0.4	62.8 ± 7.7
PP/Gd$_2$O$_3$_0.1	655 ± 22.5	49.1 ± 0.5	72.7 ± 6.1
PP/Gd$_2$O$_3$_1	689 ± 28.4	48.9 ± 0.4	67.7 ± 16.1
PP/all_0.1	686 ± 16.5	49.4 ± 0.2	83.6 ± 9.0
PP/all_0.145	697 ± 24.6	49.8 ± 0.1	64.1 ± 15.9

The strain–stress curves' results show that the Young's modulus of the system increases slightly from 10 to 30 MPa, with particle content. This increase is not significantly important compared for example to a polypropylene containing 5% of calcium carbonate particles, where the difference with an unfilled PP is around 200 MPa. As for the yield stress, the tensile mechanical tests show that it slightly decreases upon the addition of rare earth oxides particles [30, 31].

The obtained results also reveal that the elongation at break drops upon increasing the filler fraction. The decrease in the elongation at break with rigid fillers arises from the fact that the actual elongation experienced by the polymer matrix is much greater than the measured elongation of the specimen. Although the specimen is part filler and part matrix, all the elongation comes from the matrix if the filler is rigid. In the case of rare earth oxide-filled PP, there is a good adhesion between the fillers and the matrix, and thus the fracture path tends to go from particle to particle, resulting in a decrease in deformation [32].

At 0.1 wt% tracer concentration level, the elongation at break slightly decreases from 10 to 15% with a standard deviation of 6–9%. In this case the observed drop value is closed to the standard deviation of measurements and hence it can be considered that the influence of rare earth oxides is negligible.

Conclusion and Further Research

This research work demonstrated the technical feasibility of the detection of tracers dispersed in the PP matrix through the use of X-ray fluorescence spectrometry. The tracer system and detection technique used can provide specific and positive identification versatility, efficient sorting, high speed identification, high purity of the sorted fraction and solutions in dark plastics detection.

We proved that by using a test system device which allows taking static measurements of samples using energy dispersive X-ray fluorescence technology, it was possible to detect 5 of the 7 tracers tested at the concentration level of 0.1 wt% for 1 min acquisition time with a 2,000 counts/s detector.

A major parameter in the development of an industrial device is the acquisition time which must be around 10 ms. In this work, for the detection of tracers, a 2,000 counts/s detector was used. Currently, commercialized CdTe (Cadmium–Tellurium) detectors are performing under 200,000 counts/s. By using these types of detectors, the acquisition time can be reduced from 1 min to 600 ms. Moreover, in the test system proposed, no filter was used in order to reduce the noise of the signal and the measurements were done without optimising the device. To achieve the objective of 10 ms acquisition time, further work is under progress with the objective of developing a pilot plant devoted to the optimization of the concentration level of tracers and the acquisition time.

Concerning the thermal and mechanical properties of the traced PP, rare earth oxides do not seem to have a major role at 0.1 wt%. The SEM images show a homogenous dispersion of tracers in the PP matrix. More investigations are under progress in order to study the influence of rare earth oxides on the photo-degradation of the PP matrix.

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