Fluorescence labeling of polymers for automatic identification in mixed plastic waste streams. Thermal and photochemical stability.

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Abstract

Mechanical recycling of plastics saves raw materials and energy, while generating a great number of jobs, so it plays a key role in the new proposals on Circular Economy. An important concern in mechanical recycling is the identification and sorting of the different plastics, since in most cases the residues appear in mixed waste streams and the properties of the recycled material largely depend on the purity of the plastic. Therefore, in recent years a great effort has been devoted to the development of new methods for automated identification and sorting of used plastics. In this work the usefulness of different methods of identification of polyethylene based on the use of fluorescent markers is discussed. The results indicate that these methods can be very useful for the identification of plastic residues that should be removed from the waste stream for economical or health related issues. The fluorescent labeling is sensible to degradation processes, so the markers must be carefully selected in order to optimize the labeling stability.

Keywords

Waste plastics; Sorting; Mechanical recycling; Fluorescence; Labeling; Degradation.

1 Introduction

Within the set of proposals of the Circular Economy Package, the European Commission has recently proposed an ambitious increase of the targets for the recycling of plastics [1]. For instance, a common EU target for recycling 75% of packaging waste by 2030 has been suggested. Taking into account that the mechanical recycling of plastics currently stands for only less than 30 % of the waste plastics in Europe [2], the proposed objectives represent a formidable scientific and technological challenge, both for industrial companies and research centers, in order to develop new processes and technologies to increase the rates of mechanical recycling. The increase in plastic recycling rates also offers other collateral advantages such as boosting competitiveness, creating jobs and generating sustainable growth [1, 3].

To achieve an improvement in the ratio of recycled plastics it will be necessary to work on different aspects of the recycling process. One of them is the development of new technologies to improve the performance of recycled plastics, thus increasing their applications and demand and, hence, the recyclability of the waste plastics [4-7]. Another front on which progress is needed is in the separation of the collected waste plastics. It must be considered that, in general, plastics are immiscible, so that the presence of even small amounts of impurities of other plastic significantly lowers the final properties of the recycled plastic. Therefore, the insufficient separation and purification reduces the recyclability. In fact, a significant percentage of recovered waste plastics are not subjected to mechanical recycling due to the cost of the separation and purification processes required.

Nowadays, manual and automated separation processes are used. Among these we can highlight the methods based on differences in density and optical methods based on differences in the characteristic spectra of plastics, especially in the infrared. Although these methods are effective and useful, their separation capacity is in practice still far away from 100%, while recycled plastics with purities higher than 99 % are demanded for many applications. Moreover, the situation has been complicated in recent years by the emergence of products such as multilayer plastics, which are not properly separated in automated processes. Therefore, several projects have been devoted to the development of new methods to enhance the identification and sorting of plastic components in mixed plastic waste [8-11].

In recent years, several authors have proposed the use of fluorescent markers, either for the identification of different plastics waste [9-13], or to assist in the removal of a particular type of plastic, such as PET for food packaging [14]. The molecular fluorescence enables the development of cheap and robust methods for sample identification. Furthermore, it has the advantage of being a very sensitive technique so that effective detection of the tracer can be achieved with concentrations below 10 ppm in the plastic. The tracer can be introduced into the plastic either in the step of compounding, as another additive, or by applying a coating on the plastic or a fluorescent ink on a label [14].

The fluorescent markers must show strong visible emission after excitation with the most available UV lamps. The emission must be easily distinguishable from background fluorescence of commercial plastics (including additives). Furthermore, it is necessary to study the stability of the fluorescent labeling during the plastic product lifetime, as some products made from labeled plastics might be in contact with water or subjected to thermal or photochemical degradation for long periods of time before entering in the waste collection and recycle system, thus resulting in a reduction or alteration of the marker fluorescent emission. However, to the best of our knowledge too little attention has been devoted to the study of the degradation of the fluorescence of marked plastics.

Therefore, the main goal of this work was to develop a fluorescent labeling for high density polyethylene (HDPE) with improved labeling stability against thermal, hydrothermal and photochemical degradation. Such labeling can be very useful in the identification of the HDPE containers that should be removed from the waste stream. Two fluorescent markers were used, the well-known fluorescent dye rhodamine-6G (R6G) and a marker (code name: V-Quin) synthesized in the laboratory for improving integration into the HDPE and stability. Both tracers have been directly melt-compounded with HDPE in a twin-screw microextruder at concentrations below 10 ppm. In order to improve the stability of the tracer, other HDPE samples were doped with R6G supported on a layered silicate (montmorillonite). Irganox®B 900, an additive commonly used as processing and long-term thermal stabilizer, was added in all cases. The fluorescence of Irganox®B 900 and different commercial plastics and additives was previously studied in order to avoid overlap between the fluorescent emission of commercial plastics and the emission of the selected markers. The degradation of the labeled samples was characterized by using fluorescence and UV-Vis spectroscopic techniques. The modification of the layered silicate with R6G was characterized using X-Ray diffraction, Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA).

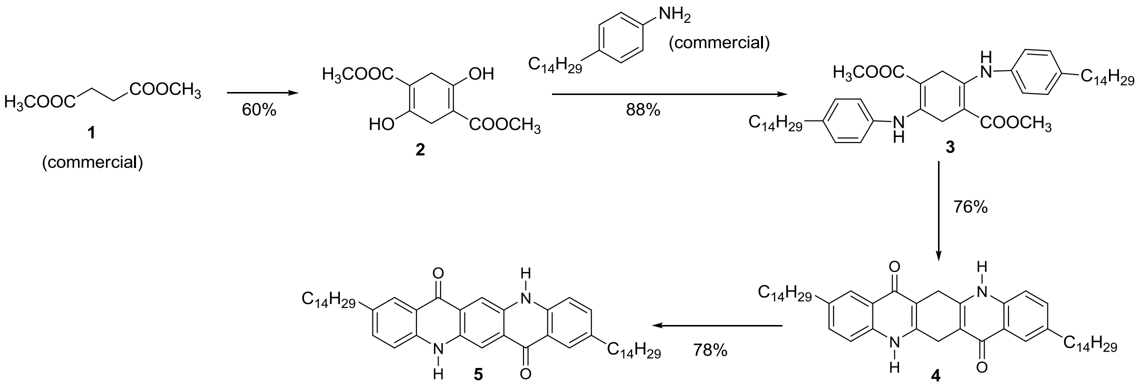
The results indicate that an efficient labeling for HDPE, with good stability, can be achieved by using properly selected fluorescent markers at very low concentrations.

2 Materials and methods

2.1 Material description and sample preparation

HDPE (number-average molecular weight of 15 kD and polydispersity index of 30.68) was supplied by Repsol®. The clay (CNa) used as marker support was a sodium montmorillonite purchased to Southern Clay Products® Inc (USA) (cationic exchange capacity equal to 92.6 meq/100 g of clay). Maleated polyethylene (MAPE, Clariant®), Irganox® B 900 (Ciba®) and $CaCO_3$ were used as additives for HDPE. The fluorescence of different additives and commercial plastics, including PVC, PET and PE, was also measured.

The marker V-Quin is a quinacridone modified with C_{14} groups in order to improve the compatibility with polyethylene chains. Quinacridones were selected due to their fluorescence emission at long wavelengths, low toxicity and high stability [15]. The main drawback of quinacridones is their low solubility in most solvents, due to the strong intermolecular interactions (π–π stacking and hydrogen bonds). However, it could be expected that the introduction of long C_{14} groups improves the solubility and stability of the marker in HDPE. V-Quin was synthesized following Scheme 1.



Scheme 1 Synthesis of quinacridone with C_{14} substituents (V-Quin)

Starting from the commercial dimethyl succinate and in four steps, the quinacridone **5** (V-Quin) was obtained. The introduction of the C_{14} could be achieved by using *p*- tetradecylaniline as the amine in the condensation step. This aniline is also commercially available. The key steps in the synthesis are the double condensation yielding compound **3** and the cyclization to afford compound **4**. As shown in the scheme, yields of all the steps are relatively high. The structure of **5** was proved by the ^{1}H NMR spectrum of a soluble derivative of **5**.

The marker V-Quin, the commercial dye rhodamine-6G (R6G) (Aldrich) and a montmorillonite modified in the laboratory with R6G (C-R6G) were used as fluorescent markers. The modification of the CNa clay with R6G proceeded as follows: the desired amount of CNa was suspended in an EtOH/H_2O mixture (80/20 V/V) and sonicated for 2 h. Then the marker was added to the reaction flask which was stirred for 24 h, sonicated for 30 min and stirred again for 1h. The solid was separated by centrifugation at 10000 rpm and washed several times with ethanol. The modified clay was dried for 24 h at 80 ^oC in a vacuum oven.

Afterwards, the HDPE samples were obtained by melt compounding in a Rondol® Microlab twin-screw microcompounder, with L/D = 20 and a screw speed of 50 rpm. The barrel temperature profile from hopper to die was 122, 150, 170, 175, 175 °C. The obtained materials were then molded by compression into films with a average thickness of 300 μm in a IQAP-LAP hot-plate press at 180 °C.

The code names of the studied materials are listed in Table 1.

Table 1. Code names and composition of the studied materials samples.

Sample	Composition
HDPE-Irg	HDPE + 0,2 w% Irganox® B900+ 1wt% MAPE
C-R6G	R6G-modified clay
HDPE- R6G	HDPE-Irg + 10 ppm R6G

HDPE- R6G-Ca	HDPE-Irg + 10 ppm R6G + 10 wt% $CaCO_3$
HDPE- C-R6G	HDPE-Irg + 0,1 wt% C-R6G
HDPE- C-R6G-Ca	HDPE-Irg + 0,1 wt% C-R6G + 10 wt% $CaCO_3$
HDPE- VQuin	HDPE-Irg + 10 ppm V-Quin

2.2 Characterization Techniques

Infrared spectra were recorded in a Nicolet iS10 spectrometer, equipped with an Attenuated Total Reflectance (ATR) accessory. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 16 scans. The fluorescence spectra were measured at room temperature with a Perkin–Elmer LS-55 luminescence spectrometer with a scanning speed of 200 nm/min. The UV-Vis spectra were measured using a Perkin Elmer Lambda 35 UV-Vis spectrophotometer, using a scan speed of 480 nm/min.

The diffraction patterns of CNa and C-R6G, before and after being modified with R6G, were obtained using a Phillips model X'Pert MPD diffractometer, equipped with a CuKα generator (λ = 0.1542 nm) at 45 kV and 40 mA, in a 2θ range from 2 to 40 °. The thermogravimetric analysis of the same materials was carried out using a TA Instruments TGA2050 thermobalance. Samples of 10–20 mg were heated at 10 ^oC/min from room temperature to 900 ^oC in dry nitrogen (30 cm^3/min).

2.3 Degradation processes

The samples of HDPE labeled with V, R6G and C-R6G were submitted to different degradation processes in severe conditions in order to study the durability of the labeling. Thermal and hydrothermal degradation were carried out at 80 ^oC in an oven and in deionized water, respectively. The photochemical degradation was carried out at 40 ^oC in an Atlas UVCON chamber, equipped with eight F40UVB lamps, for 100 h.

3 Results and discussion

3.1 Fluorescence of commercial plastics

Fluorescent markers selected for automatic identification and separation of plastics in mixed waste streams must meet certain conditions, which have been reviewed by several authors [9-14]. Among the required conditions, the following can be highlighted:

- The fluorescent tracer must be easily incorporated into the plastic, in this case HDPE.
- The marker must be non-toxic and migration from the plastic to the environment must be minimal.
- The tracer must be stable at the processing temperature of the plastic.

- The fluorescence emission intensity should be high enough to keep the concentration of tracer to a ppm level, so as not to affect the properties of the plastic.
- The tracer must be compatible with all components of the plastic, including other additives and fillers.
- Considering that commercial plastics will be subjected to ambient conditions for a time which can be long, the fluorescent labeling must be resistant against thermal, hydrolytic and photochemical degradation.
- The tracer chosen should show a fluorescent emission that is clearly distinguishable from the emission of the unmarked plastic and also from the fluorescence of all other plastic that can be found in the stream of mixed waste. This condition also includes the fluorescence of additives that can be found in plastics. It should be noted that some widely used commercial plastics contain additives with a significant fluorescent emission, such as optical brighteners.

Taking into account the last condition, the fluorescence of commercial plastics that can often appear together with HDPE in mixed waste streams was measured. Fig 1 shows the emission observed in different commercial samples of PVC. The three samples have an appreciable fluorescence emission, although the intensities and wavelengths are clearly different. Sample 2 shows a very intense emission indicating the presence of a fluorescent additive. Sample 3 corresponds to naturally aged PVC and shows emission bands at longer wavelengths due to the products generated during environmental degradation [16]. This result indicates that the fluorescence of commercial plastics depends not only on the presence of additives, but also the aging of the material.

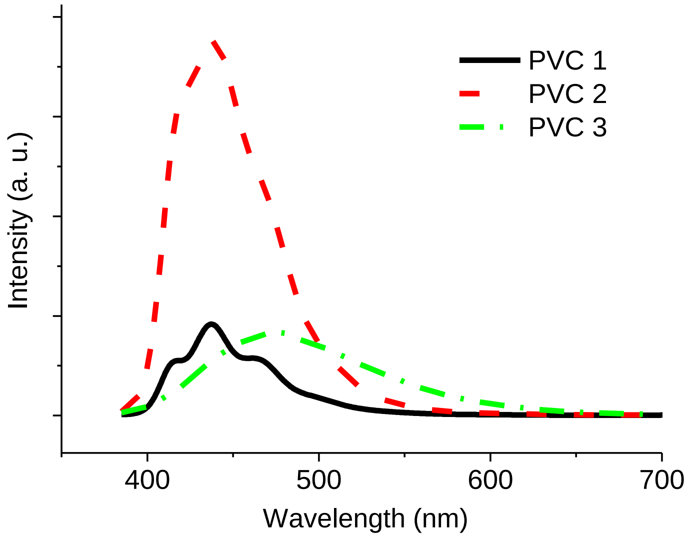


Fig. 1 Fluorescence emission spectra (λ_{ex} = 350 nm) corresponding to three commercial samples of PVC

Fig 2 shows the spectra of commercial samples of poly(ethylene terephthalate) (PET) and low density polyethylene (LDPE). While LDPE does not show significant fluorescence, the PET sample shows an appreciable emission centered at 410 nm, in good agreement with the spectra reported by Itagaki and Kato [17].

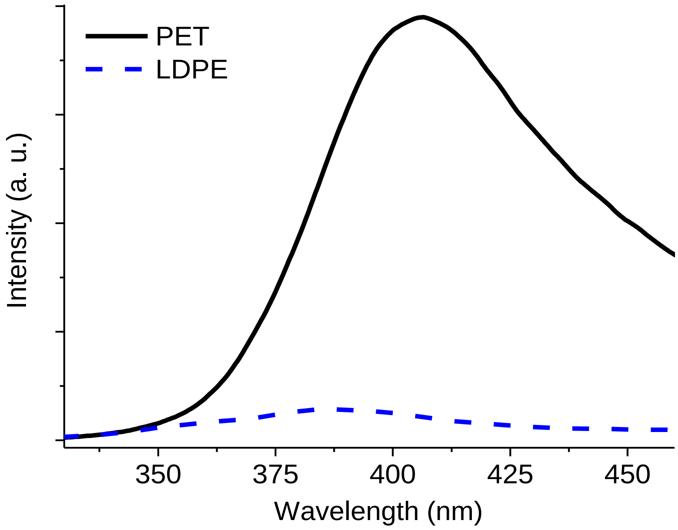


Fig. 2 Fluorescence emission spectra (λ_{ex} = 290 nm) corresponding to commercial samples of PET and LDPE

It has been also observed that some additives widely used in commercial plastics possess significant fluorescence. Fig 3 shows the fluorescence emission of an acetone solution of Irganox® B 900, an additive commonly used as a stabilizer for polyolefins and other plastics. The emission spectrum of a HDPE sample containing 0.2 wt. % of Irganox® B 900 is also shown.

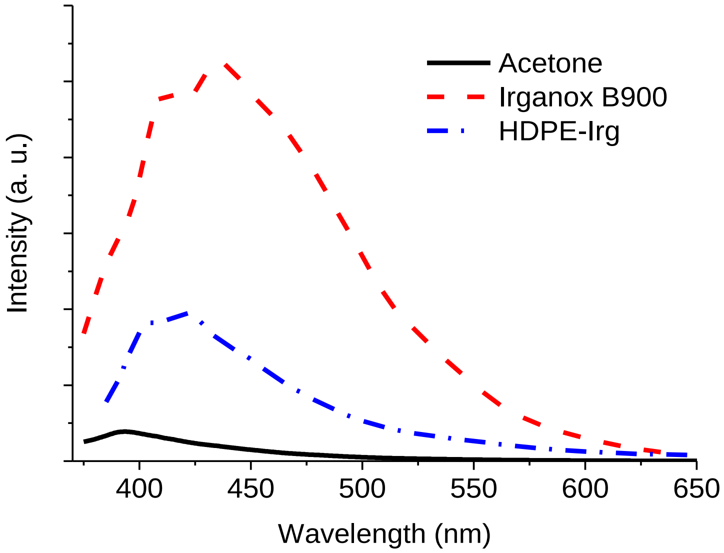


Fig. 3 Fluorescence emission spectra (λ_{ex} = 350 nm) corresponding to Irganox® B 900 (solution in acetone) and the HDPE used in this work (0.2 wt % of Irganox® B 900)

Thus, the obtained results show that some widely used plastics and, especially, some additives, show a significant fluorescence emission between 400 and 500 nm when they are excited with conventional UV lamps, such as those expected in the automated detection systems for plastics with fluorescent labels. This fluorescence emission would interfere with the fluorescence of the tracer, so it is necessary to select tracers with fluorescent emission well above 500 nm. The two markers selected for this work meet this requirement.

3.2 R6G-modified montmorillonite

One objective of this work was to compare different ways of introducing the fluorescent marker into the plastic. Therefore R6G has been introduced into HDPE in two ways, either directly or immobilized in a layered silicate (sodium montmorillonite, CNa). The immobilization process has been described in detail in the experimental part.

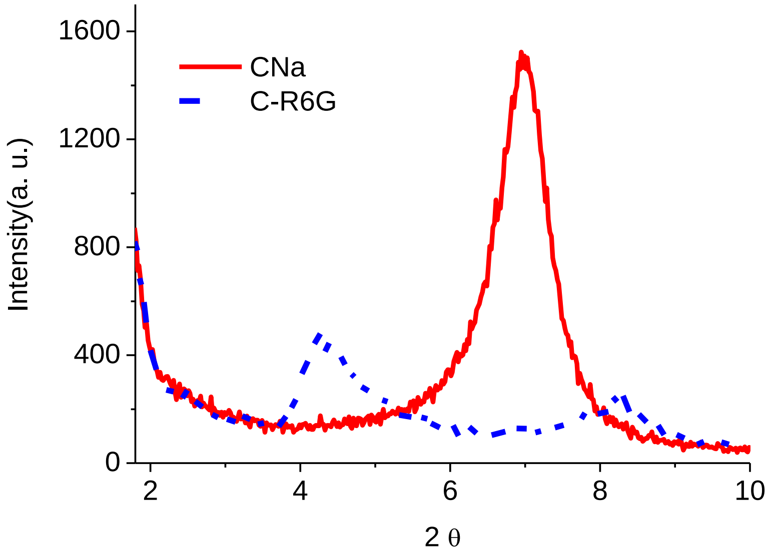


Fig. 4 XRD traces corresponding to unmodified clay (CNa) and CNa modified with R6G

Fig 4 shows the XRD patterns of the pristine CNa and the R6G-modified clay (C-R6G). It can be seen that the characteristic (001) diffraction peak of pristine clay appears at 2θ = 7^0, wich corresponds to a basal spacing of 12,6 Å, calculated according to the Bragg equation [18]. The treatment of the clay with R6G until a 100% of their cationic exchange capacity causes a shift of the (001) diffraction peak toward lower diffraction angle (2θ = $4{,}3^0$) that corresponds to a higher basal spacing (20,5 Å). This expansion of the interlayer space reveals the correct intercalation of R6G between the nanosheets of the clay. A very similar basal spacing has been previously reported for montmorillonite treated with R6G [19].

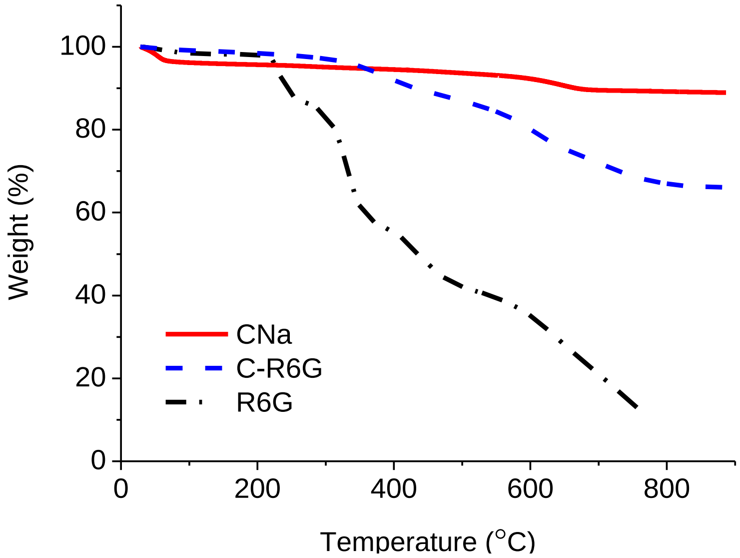


Fig. 5 Thermogravimetric traces corresponding to unmodified clay (CNa), R6G and CNa modified with R6G

Fig 5 shows the thermogravimetric curves (measured in dry nitrogen) of CNa, R6G and C-R6G. The small weight loss observed in the pristine clay at low temperatures is due to the evaporation of surface water. The weight loss appearing at temperatures higher than 600 °C can be assigned to the dehydroxylation of the aluminosilicate structure [18]. The thermogravimetric trace of R6G reveals that this compound is thermally stable up to 220 °C and then presents several weight losses corresponding to degradation processes. However, it must be highlighted that the curve corresponding to C-R6G does not show any significant weight loss below °C. This is an interesting outcome as it entails that immobilized R6G has greater thermal stability than the neat dye, thus indicating that the immobilized fluorescent tracer will suffer a less important thermal degradation during the melt processing with HDPE, which is performed at temperatures near 200 °C.

3.3 Fluorescence and stability of labeled plastics

The chosen tracers (R6G, C-R6G and V-Quin) were incorporated into HDPE by melt processing with the aim of characterizing the fluorescence of the labeled plastics and study the stability of that fluorescence during photochemical, thermal and hydrothermal degradation processes.

Fig 6 shows the fluorescence emission of HDPE containing different additives and fillers. All samples contain 0.2 wt% of Irganox® B 900. The presence of R6G explains the appearance of a strong emission band with maximum at 567 nm, which enables an easy detection of plastics labelled with rhodamine, even with only 1 ppm of tracer. One of the samples labeled with R6G also contains 10% by weight of $CaCO_3$, an additive commonly used as filler in HDPE. The presence of $CaCO_3$ modifies the emission spectrum of R6G, causing a shift of the maximum to 561 nm and a marked decrease in the observed intensity. This decrease can be explained by considering that the filler favors non-radiative deactivation processes, thus reducing the efficiency of the fluorescent emission. Moreover, it must be considered that the filler decreases the light transmission of the plastic, thereby decreasing the excitation of R6G fluorescence. However, it should also be noted that the fluorescence of the tracer remains readily detectable in the $CaCO_3$ filled plastic, even with tracer concentrations near 1 ppm.

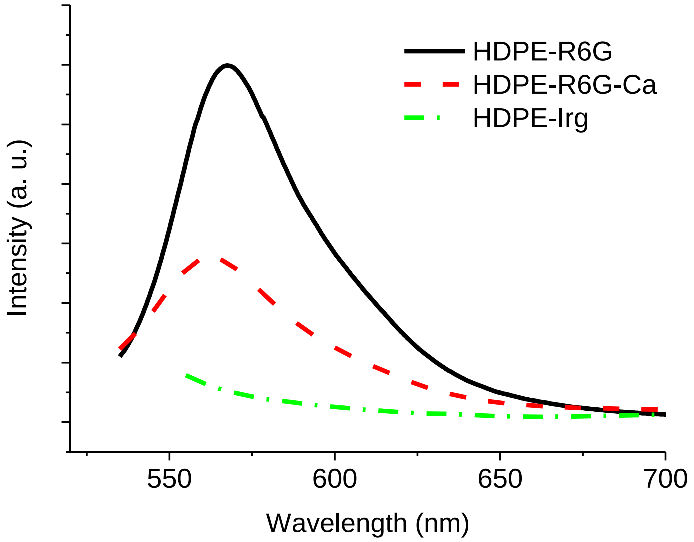


Fig. 6 Fluorescence emission spectra (λ_{ex} = 510 nm) corresponding to HDPE labeled with R6G (10 ppm, solid line), HDPE labeled with R6G and containing 10 % by weight of $CaCO_3$ (dashed line) and to unlabeled HDPE (dash dot)

The use of clay to protect the tracer inside the plastic causes significant changes in the fluorescence emission spectra, as shown in Fig 7. While the emission of the fluorophore directly compounded with HDPE shows a maximum at 560 nm, the emission spectrum of HDPE labeled with R6G-modified montmorillonite shows a maximum centered at 583 nm with a definite shoulder at 560 nm. A similar shift has been previously observed by other authors in rhodamines incorporated in layered silicates such as laponite [20]. This shift may be explained as a result of the formation of dimers and other aggregates of R6G inside the clay. In general, the incorporation of fluorophores in the rigid structure of the clay increases the fluorescence quantum yield; however, the formation of aggregates reduces the fluorescence efficiency. The shoulder appearing at 560 nm in the emission spectrum may correspond to the presence into the marked plastic of R6G extracted from the clay during the melt extrusion process.

Fig 7 also shows that the exposition of the marked plastic to UVB light reduces the fluorescence emission intensity, probably because the R6G found near the surface of the plastic is destructed in a photochemical process. The spectrum of the photodegraded plastic shows the maximum at 583 nm with the shoulder at 560 nm, with no significant shifts in the emission wavelengths caused by the photochemical degradation. A weak emission appearing at longer wavelengths in the spectrum of the photodegraded plastic may reveal the formation of weak fluorophores during the photodegradation of R6G.

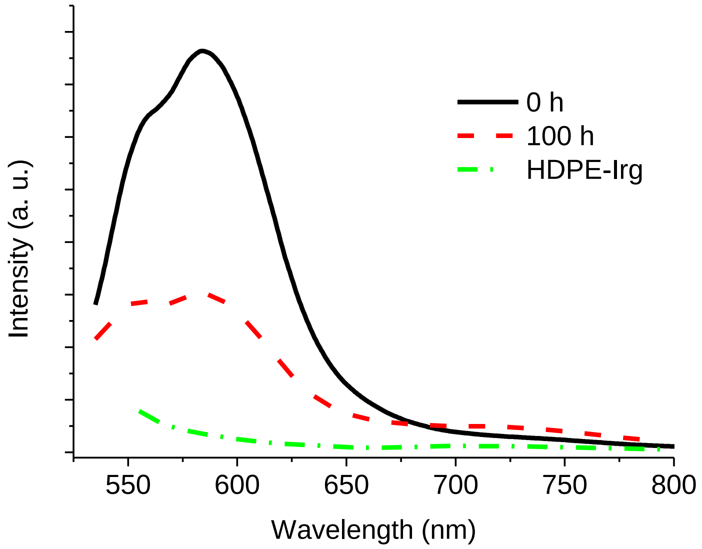


Fig. 7 Fluorescence emission spectra (λ_{ex} = 510 nm) corresponding to HDPE (with 10 wt% of CaCO3) labeled with R6G-modified clay, measured before (solid line) and after (dashed line) 100 h of photochemical degradation

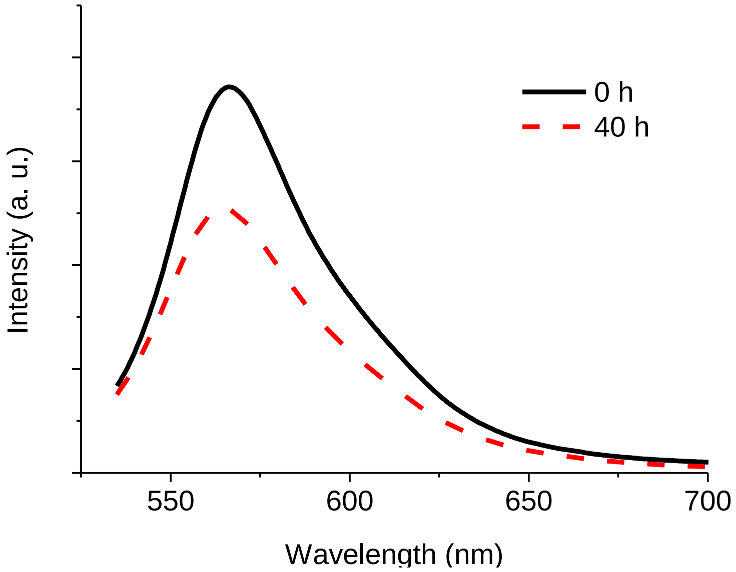


Fig. 8 Fluorescence emission spectra (λ_{ex} = 510 nm) corresponding to HDPE labeled with R6G before (solid line) and after (dashed line) 40 h of thermal treatment at 80 ^{o}C

Despite the decrease in emission intensity caused by exposure to UVB light, the marked plastic shows good resistance since the emission of the tracer is clearly observable and distinguishable from that of unmarked plastic even after 100 hours of exposure in certainly aggressive conditions. A similar result was obtained during the study of the thermal degradation at 80 °C of the marked plastics (see Fig 8). HDPE marked with R6G shows retention of near 70 % of the emission intensity after 40 hours of thermal treatment. The spectrum of the tracer is clearly identifiable and only a small shift of the peak from 565 to 563 nm was observed.

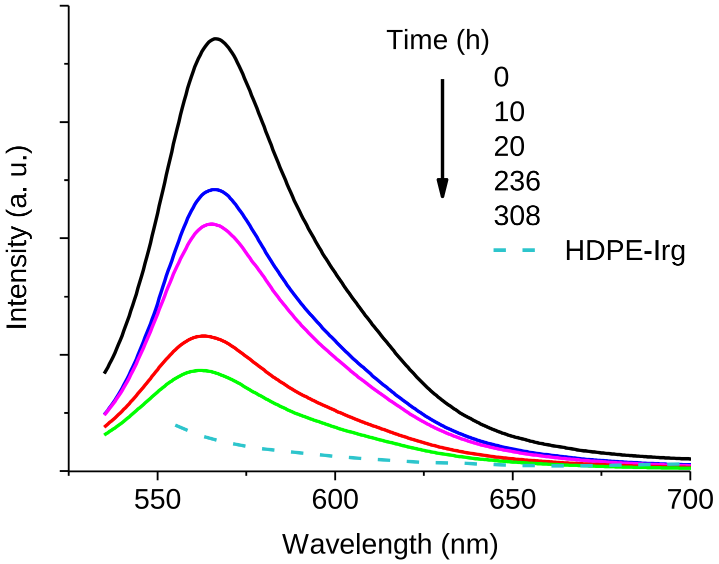


Fig. 9 Evolution of the fluorescence emission of HDPE-R6G (λ_{ex} = 510 nm) during the hydrothermal degradation

In order to study the effect of water on the degradation of the fluorescence emission, the marked plastics were subjected to accelerated hydrothermal degradation in deionized water at 80 °C. Fig 9 shows the time evolution of the fluorescence emission spectra of HDPE marked with neat R6G. The hydrothermal degradation causes greater decreases in the fluorescence intensity than the thermal degradation at the same temperature in absence of water, since a decrease of almost 50 % of the emission intensity is observed after only 20 hours of degradation. However, the labeling can be considered again as stable, since tracer emission is clearly distinguishable after more than 300 hours of degradation. The spectra show a small shift of the emission peak from 565 to 561 nm.

The effect of water on degradation has been explained as the result of a lixiviation process, since the medium facilitates the extraction of the tracer from the plastic. To test this hypothesis, the spectra and the time evolution of the fluorescence of the immersion media were measured and compared to the emission of the marked plastic. It was found that the emission spectrum of the medium is very similar to the spectrum of R6G, thus revealing the presence of extracted R6G in the medium. In addition, the comparison of the two time evolution traces, shown in Figure 10, clearly suggests that there is a relationship between the emission decrease of plastic and the emission increase of the medium.

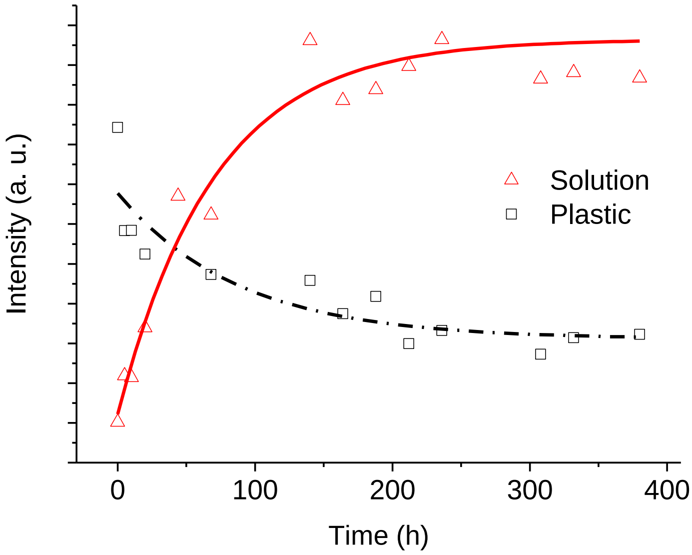


Fig. 10 Time evolution of the emission intensity (λ_{ex} = 510 nm) of HDPE marked with R6G and its immersion medium during the hydrothermal degradation

The above results indicate that the lixiviation contributes to the degradation of the fluorescence of the marked plastics and suggest that the stability of the labeling can be enhanced by selecting markers with better anchoring in the plastic. Fig. 11 allows the comparison of the lixiviation of R6G and R6G incorporated inside the layered silicate. As expected, encapsulation of the fluorophore in the clay clearly reduces the effect of the leaching.

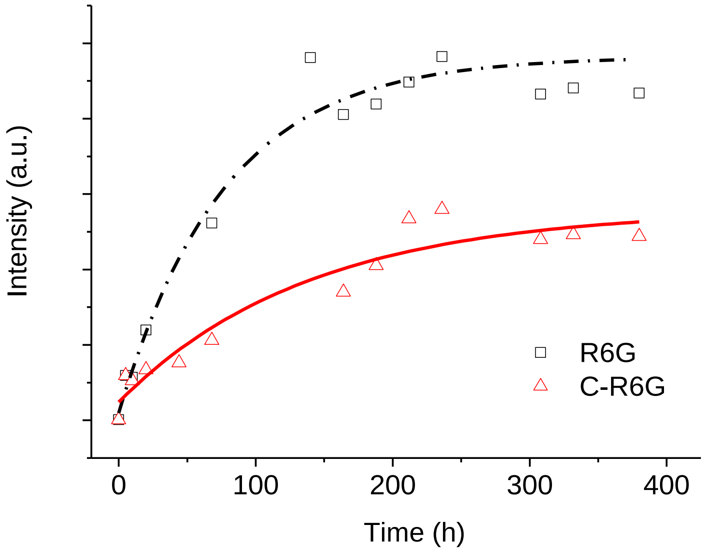


Fig. 11 Time evolution of the emission intensity of the immersion media (λ_{ex} = 510 nm) during the hydrothermal degradation of HDPE marked with R6G and R6G-modified clay

Bearing in mind this issue, the marker V-Quin was developed by its stability and to improve anchoring in polyethylene. Figure 12 shows that this tracer has an intense and characteristic fluorescent emission at wavelengths higher than 550 nm, which is clearly distinguishable from the emission of the unmarked plastic, making it suitable for fluorescent labeling of plastics such as HDPE. The emission decreases during degradation, but this marker shows greater stability than R6G, since the emission decreases only 60% after more than 300 hours of hydrothermal degradation. Moreover, the shape of the spectrum is almost invariant during the degradation and the signal is clearly noticeable after 308 hours of hydrothermal degradation. The greater stability of HDPE marked with V-Quin can be also observed in Fig 13, where the relative retention of the emission during the hydrothermal degradation of HDPE-R6G and HDPE-V-Quin is compared.

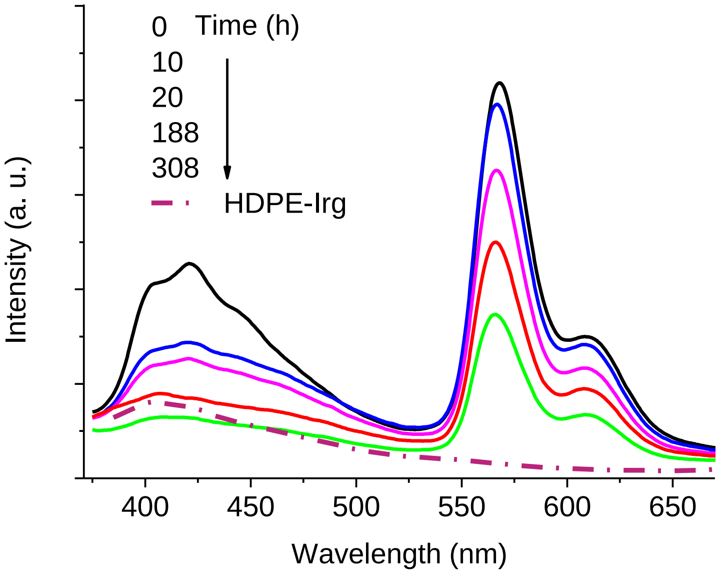


Fig. 12 Evolution of the fluorescence emission of HDPE marked with V-Quin (λ_{ex} = 350 nm) during the hydrothermal degradation

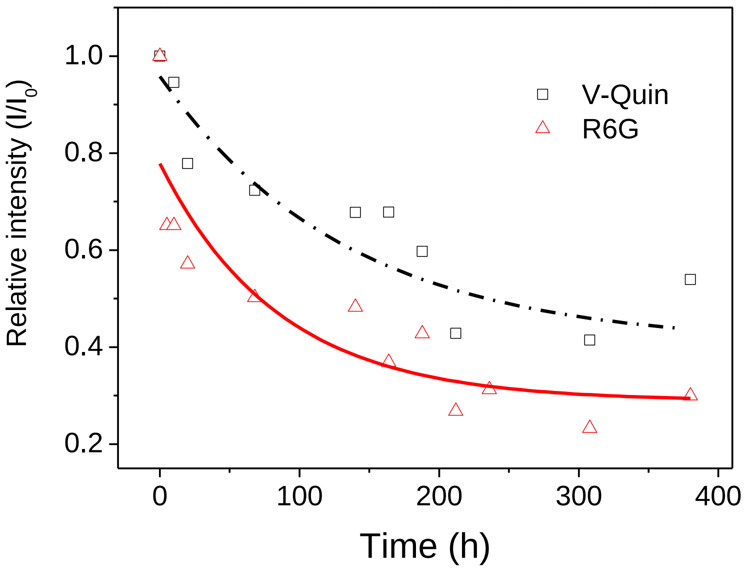


Fig. 13 Retention of the fluorescence emission of HDPE marked with R6G and V-Quin during the hydrothermal degradation

The above results indicate that a proper selection of the fluorescent labeling process for each polymer will enable the identification of the marked plastic even after the different degradation processes that might affect the product during its lifetime.

4 Conclusions

The fluorescent labeling of HDPE can be very useful to enable the identification of residues of this plastic that should be eliminated from mixed plastics waste streams, in order to facilitate the mechanical recycling of these streams. It has been analyzed the fluorescence of HDPE marked with rhodamine-6G and V-Quin (a new tracer developed by us) and the stability of the fluorescent labeling during different processes of photochemical, thermal and hydrothermal degradation. The results indicate that very stable fluorescent labeling of HDPE is possible through simple and inexpensive processes. The good stability of the fluorescent emission indicates that the marked plastics will be properly identified after their lifetime. The immobilization of rhodamine-6G in a layered silicate reduces the leaching of the tracer, thus improving the resistance of the labeling against the hydrothermal degradation. V-Quin shows better stability and better anchoring to polyethylene than rhodamine-6G.

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