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Photoluminescence spectroscopy on commercially available plastic products

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Abstract Commercially available plastic products are produced for specific applications. They represent polymeric compounds, i.e. base materials mixed with various types of additives such as pigments. The identification of the plastic type is the key goal in microplastics analysis but also the key process when it comes to recycling macroscopic plastic litter. Established methods to analyze microplastic particles are FTIR spectroscopy and Raman spectroscopy. Both methods have shortcomings regarding plastic size and measurement speed. In 2020 Ornik et al. demonstrated that polymeric base materials can be differentiated from natural materials using photoluminescence spectroscopy. Here, we extend this method by examining commercial polymeric packaging materials found in the supermarket, which are colored by different pigments.

Keywords:

Microplastics, photoluminescence, detection technique, detection limits

1. Introduction

Considering the versatility in the properties of plastics, the global production market started to replace wood and metal production with plastic production since the beginning of 19th century (Feldman, 2008). Due to the inefficiency of plastic waste management systems, worldwide, about 72% of plastic is mishandled (Team from Ellen MacArthur Foundation, 2016). This mishandled plastic waste eventually enters into the marine and terrestrial environment. It has been reported that several plastics take more than 100 years to degrade (Jambeck et al., 2015; Ohtake et al., 1998). Moreover, the presence of plastic litter (microplastic/macroplastic) in the environment could be harmful considering the additives and POP's present in them (Hahladakis et al., 2018). It is therefore necessary to identify and trace out the origin of plastic added into the environment. Widely used plastic identification methods are FTIR and Raman spectroscopy (Hanvey et al., 2017; Jung et al., 2018; Prata et al., 2019). Both measurement techniques are slow and cost-intense in terms of equipment.

In 2020, Ornik et al. reported on first experiments to explore the potential of photoluminescence (PL) spectroscopy to detect microplastics as this technique is potentially fast and cost-efficient (Ornik et al., 2020). Ornik and coworkers studied a set of nine bulk base polymers. Here, we extend this study, by examining the impact of a variety of additives on the PL spectra. Additives, such as pigments are typically found in the plastics of commercial products.

2. Materials and methods

2.1. Materials

We have collected different Resin identification code (RIC) labeled plastic products from household waste. We chose to investigate four out of the six most commonly produced plastics (PET, HDPE, LDPE, PP) in Germany (Heinrich-Böll-Stiftung, 2019). We were able to procure a few colorless and colored RIC labeled polymers: white, black/grey, blue, red/pink, yellow/green. Reference colorless base polymers were procured from Bretthauer GmbH, Germany. Furthermore, to evaluate the differentiation limits in terms of microplastic segregation, eight different natural materials often found a beach environment were examined: eggs of sea snail (Hexaplex trunculus), sea snail shells (Monodonta turbinate), coralline red algae (Lithophyllum racemus), sea urchin skeleton (Echinocardium cordatum), wood with teredo, wood, sea grass leaf (Posidonia oceanica), and fine-grained quartz sand (Knauf Bauprodukte GmbH)

2.2. Experimental setup and methods

A blue laser diode emitting light at 405 nm with a power of 175 mW is used as an excitation source. A 405 nm bandpass filter is placed right after the laser to block emissions of the laser at other wavelengths. The beam then passes through a 425 nm dichroic mirror which reflects the excitation beam towards the sample and allows only the emissions beyond 425 nm to transmit towards the detector. Lens-1 focuses the laser beam onto the sample and simultaneously collimates the PL emitted from the sample. The collimated PL then passes through an additional 420 nm long pass filter and then onto lens-2 which focusses the PL signal into a multimode optical fiber which guides the emission into a spectrometer (LR2 from Lasertack). To avoid any interference of emission channels of sample and substrate, a silicon wafer was chosen as a substrate for all the measurements as it does not emit fluorescence in the visible region.

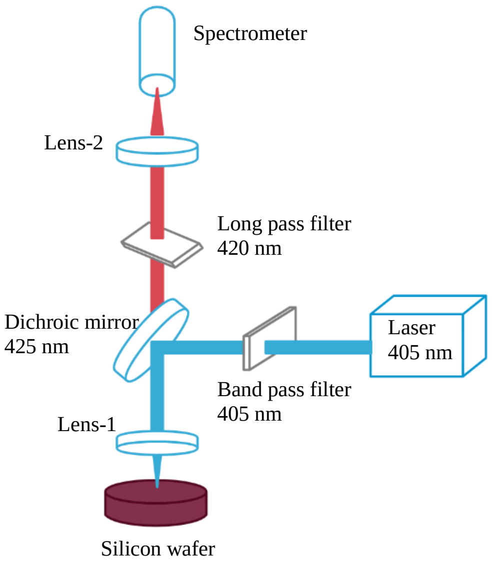

Figure 1. Schematic of the experimental setup used to detect PL emissions. The excitation path is represented by the blue channel while the red channel represents the emission path.

3. Results & discussion

Figure 2 shows the PL spectra of all the examined polymers and natural materials. As already reported by Ornik et al., the broad emission bands of base polymers (white dashed line) are accompanied by Raman peaks around 460 nm, which are attributed to C-H and CH_2 modes (Edwards, 2005; Ornik et al., 2020). The position of the Raman peak depends on excitation wavelength and power.

Depending on the additive and the pigment added to the plastic product, the PL spectra of RIC labeled polymers (solid lines) differs from their respective base polymers (dashed lines). However, the emission band until 470 nm displays significant similarities with the base polymer, which also includes the Raman peak. Especially in case of yellow and red colored samples the pigment emission band dominates the polymer specific emission band. Most of the black polymer samples show very weak luminescence but a few show a luminescence spectrum which resembles that of the base polymers. Clearly, a further more detailed investigation is necessary to understand the influence of additives and pigments on the luminescence spectra. Yet, this is out of the scope of this paper.

As shown in Figure 2, all the natural materials examined in this study show emission maxima beyond 470 nm and the polymers show their significant bands around 435 and 450 nm. To classify polymers and natural materials we exploit these spectral features by defining two parameters as defined below:

$$\boldsymbol{P_1} = \boldsymbol{\lambda[\text{1st peak}]} \qquad \boldsymbol{P_2} = \frac{\int_{430\ \text{nm}}^{440\ \text{nm}} \mathbf{I(\lambda)\ d\lambda}}{\int_{455\ \text{nm}}^{465\ \text{nm}} \mathbf{I(\lambda)\ d\lambda}}$$

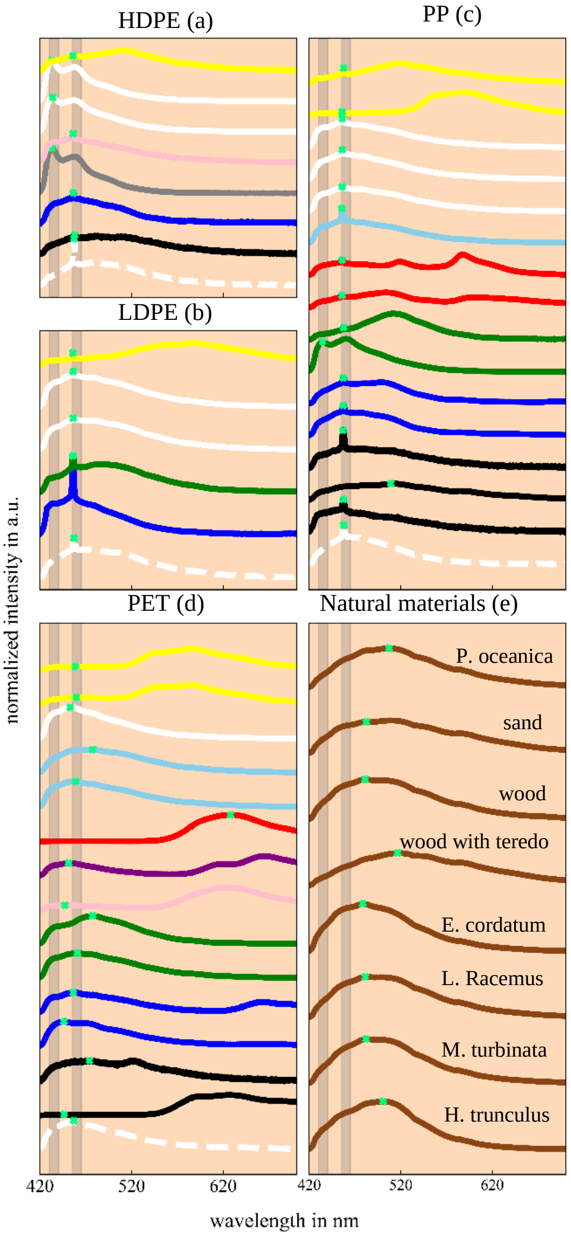

Figure 2. Normalized PL spectra of polymers HDPE (a), LDPE (b), PP (c), PET (d) and natural materials (e). All the spectra are stacked with an equal offset. All the solid lines represent RIC labeled polymer samples, the line color represents their respective colors except for transparent samples which are represented by sky blue solid lines. The white dashed lines indicate the base polymers from Bretthauer. The vertical shaded regions inidcate the region of analysis and the lime green stars indicates the first peak maxima.

Parameter P_1 is based on the first peak wavelength (i.e. the peak with the shortest wavelength) as indicated by lime green stars in Figure 2. Parameter P_2 is ratio between two areas under the curve indicated by the grey shaded regions in Figure 2. These two regions were chosen considering the strongest features in base polymer compared to natural materials.

Referring to Figure 3, we notice the formation of three clusters. Most of the polymers have smaller P_1 values smaller than that of the natural materials. The data points of the polymers form two clusters which slightly overlap.

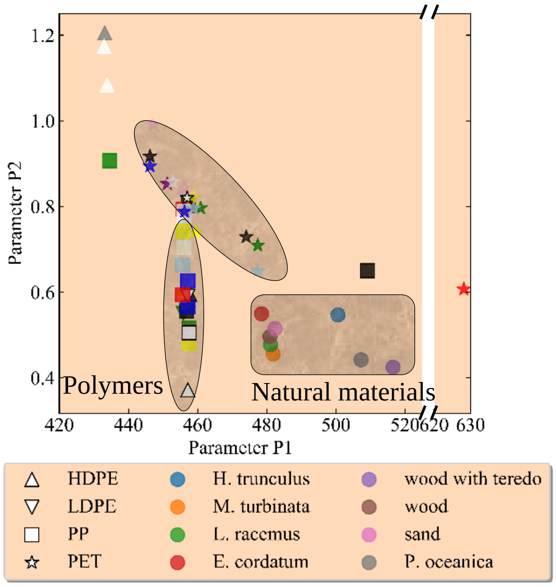

Figure 3. Parameters P_2 as a function of P_1. Circles represent natural materials. The polymers are represented as indicated in the legend. The white fill-black borderd marker indicates base polymers from Bretthauer, the rest of the markers represent their respective colors except for colorless which is represented by skyblue.

The P_2 values of most of the PET samples are larger than the P_2 values of LDPE, HDPE and PP. P_1 values of LDPE, HDPE and PP fall in the same region due to an identical Raman peak. Two black PP samples were measured. The data point for one of them falls appropriately in the polymer cluster due to the presence of the Raman peak. The spectrum of the other sample did not show a Raman peak, therefore a relatively large P_1 value. For the red PET the pigment luminescence is dominating. This completely screens the luminescence form the base polymer. It's luminescence, hence, peaks at 628 nm. The rest of the outliers in Figure 3, the two white and one grey HDPE (Figure 2a), and one green PP sample show similar emission bands (Figure 2c), probably to an identical additive. Yet, their luminescence spectra are completely different from that of the respective base polymers.

4. Conclusion

Using PL spectrosocpy the identification of polymer type in presence of additives and pigments might be challenging to achieve. Nevertheless, we demonstrate the possibility of differentiating commercial plastics from natural material separation. Taking the cost and simplicity of PL spectroscopy into account, this kind of differentiation is sufficient as a cheap first analysis method. This could be useful for systems for field analysis or even for affordable microplastic removal systems.

In terms of polymer type identification, further detailed investigation is necessary to understand the influence of additives on the PL spectra of polymers. Advanced machine learning algorithms could also be used by providing the information on the pigment and additives to train the prediction model.

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