Recycling of Waste Polymethyl-Methacrylate as an Optical Transparent Host

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Abstract: Reusing waste or otherwise discarded polymethyl methacrylate (wPMMA) as a host matrix for optical photonic applications such as down-conversion or luminescence solar concentrators can spare the use of pristine materials, with strong implications for sustainability. Here, a homogeneous emissive film was produced using wPMMA by dissolving in toluene and adding a fluorescent perylene dye (perylene-3,4,9,10-tetracarboxylic hexyl ester, PTHE) followed by spin coating casting. This resulting film is optically transparent and green-emissive with a high photoluminescence quantum yield (PLQY of 84%). It has been investigated by various spectroscopic techniques such as absorption, photoluminescence, emission lifetime, and dye photostability. While this film exhibited some excimer PL at longer wavelengths compared to the solution phase, it also increased its emission lifetime by approximately 3 times. Moreover, while the CIE coordinates (x, y) of the blue-green PL in the solution phase was 0.21, 0.56, the PL spectrum of the wPMMA:PTHE film instead had (CIE, x, y) of 0.30, 0.60. Recycling these and similar suitable waste polymers and transforming them into value-added products such as down-conversion or luminescent solar concentrator films can contribute to sustainable development goals within the scope of clean energy, energy efficiency, and waste utilization.

Keywords: Waste polymethyl methacrylate, optical host, recovery of waste polymer, solid-state lighting, luminescence solar concentrator, perylene dye.

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1. INTRODUCTION

Plastics are a wide category of synthetic materials composed of chains or networks (polymers) of repeating smaller building blocks (monomers). Plastics typically possess exceptional versatility, allowing them to be shaped into various forms without compromising on durability, flexibility, lightweight nature, or affordability. They also enable composite production with adjustable structural and physical properties depending on different synthetic substitutions or blending with other materials (1-4). This remarkable adaptability has supported plastics finding applications in a wide range of industries since the mid-20th century, spanning from automotive and packaging to electronics and medical device manufacturing (5-8). While plastic production and usage have grown exponentially in recent decades - estimated to reach approximately 400 million tons per year – the product lifecycle of these materials is not fully developed. Approximately 12% of plastic production is disposed of by incineration, and only approximately 9% is recycled despite their chemical suitability for reuse (9). Hence, while plastics serve numerous useful purposes in modern society, most of the plastics produced remain discarded in nature for hundreds of years following use (a result of their chemical stability). This pollution contaminating environments and water resources is now an urgent environmental problem that must be addressed (10-12). Hence, efforts to recycle rather than discard plastics not only contribute to the protection of environmental and human health but also contribute to a sustainable future in terms of protecting natural resources, saving energy, combating climate change, and managing economic outputs and waste (4,13,14).

Polymethyl methacrylate (PMMA), also known as acrylic glass, is a thermoplastic polymer obtained by polymerization of methyl methacrylate (MMA) monomer (5). PMMA is used in many different areas, such as furniture, building facades, lighting
fixtures, automobiles, contact lenses, chemical tanks, and optics and photonic technologies (15). In photonic technologies specifically, PMMA is used extensively in roles such as light transport in optical fibres, eyeglasses, and telescope lenses, LCD (liquid crystal display) and LED (light emitting diode) screen protectors, dye hosts for light conversion layers in blue LEDs, and optical filter production (5,7,16-24). All these features and application areas make PMMA an important plastic group in this technological field. However, PMMA has low biodegradability in waste environments, and its production processes have several environmental impacts to consider - such as the necessity of using water in its production, the production of MMA from oil and natural gas, and energy consumption – which establish the importance of PMMA recycling and (re)use.

Perylene derivatives are known for their strong light absorption in the visible region and high fluorescence quantum yields. In addition, since they exhibit high optical, electrochemical, and thermal stability, perylene dyes are used in many optical or optoelectronic technologies such as (organic) light emitting diodes (LEDs and OLEDs), organic solar cells (OSC), luminescent solar concentrators (LSC), lasers, ion sensing, and phototherapy (25-34). Perylene tetracarboxylic dianhydride (PTCDA), 1-hexanol, 1-bromohexane, N,N-dimethylformamide, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), N,N-dimethylformamide, chloroform, toluene, silica gel and thin layer chromatography (TLC) were obtained from Sigma and Merck. The waste polymethyl methacrylate (wPMMA) used in this study (Figure 1, picture on the right) was obtained as waste from a laser-cutting stationery shop. PTHE was synthesized (Figure 2) according to the literature (21,41). The synthetic details are provided below, together with its structural, thermal, and optical characterizations.

In this study, we show that waste/discarded PMMA polymer (wPMMA) can be reclaimed as an optically transparent host for Perylene-3,4,9,10-tetracarboxylic hexyl ester (PTHE), doped at 1 wt% and with optoelectronic applications as outlined above. Due to the environmental and economic impacts of waste polymers, this technique can contribute to the Sustainable Development Goals (40) and reduce the need for additional PMMA production from petrochemicals. PTHE and the dye-loaded films were characterized by FTIR, ¹H-NMR, ¹³C-NMR, HRMS, TGA, XRD, and optical spectroscopy. PTHE exhibited extremely high PL intensity and PLQY when homogeneously dispersed in the organic-compatible wPMMA, with excellent stability towards photodegradation. The PTHE:wPMMA film (or others like it) can hence be used as an environmentally friendly material feedstock in the production of white light-emitting (O)LEDs or other photonics applications.

2. EXPERIMENTAL SECTION

2.1. Materials and Instruments

Perylene tetracarboxylic dianhydride (PTCDA), 1-hexanol, 1-bromohexane, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), N,N-dimethylformamide, chloroform, toluene, silica gel and thin layer chromatography (TLC) were obtained from Sigma and Merck. The waste polymethyl methacrylate (wPMMA) used in this study (Figure 1, picture on the right) was obtained as waste from a laser-cutting stationery shop. PTHE was synthesized (Figure 2) according to the literature (21,41). The synthetic details are provided below, together with its structural, thermal, and optical characterizations.

FTIR-ATR, ¹H, and ¹³C NMR spectra were obtained using IRaffinity-1 SHIMADZU-FTIR and Bruker (400 MHz and 100 MHz) spectrometers, respectively. TGA analysis was carried out with a Hitachi STA 7300 Model device with an increase of 10 °C per minute in a nitrogen atmosphere. Absorption and photoluminescence (PL) spectra and PL quantum yield (PLQY) were performed with the Analytical Jena S600 UV–Vis spectrophotometer and Edinburgh FLS920P and FS5 Instruments.

2.2. Synthesis and Characterization of Perylene-3,4,9,10-tetracarboxylic hexyl ester (PTHE)

Perylene tetra esters emit with very high fluorescence efficiency in the solution phase (PLQY≥90%) (42). Therefore, in this study, PTHE was chosen as a reference fluorophore. Detailed information on the synthesis methods and
characterization of PTHE (Figure 1) and wPMMA:PTHE film (Figure 2) are given below (Figure 1-10).

**Figure 2:** Reaction scheme of PTHE.

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (1 g, 2.55 mmol), N,N-dimethylformamide (DMF), 1-bromohexane (4.2 g, 25.5 mmol) and 1-hexanol (2.6 g, 25.5 mmol) were added into a two-necked round-bottomed flask. After it was stirred for 20 minutes in a magnetic stirrer, the DBU (1.5 mL) catalyst was added and stirred at 80 °C under reflux in N₂ for 24 hours. After the flask was brought to room temperature, it was poured into distilled water, and the precipitate was filtered through vacuum filter paper and washed with methanol. After drying the solid at 60 °C, it was dissolved in chloroform and purified by column chromatography over silica gel. Yield (79%) 1.54 g.

**FTIR (ATR) (Figure 3):** \( \tilde{\nu}_{\text{max}} = (\text{C}_\text{Ar}-\text{H}): 2951, 2928 \text{ cm}^{-1}, (\text{C-H}): 2864, 2848 \text{ cm}^{-1}, (\text{C=O}): 1726, 1710 \text{ cm}^{-1}, (\text{C-O}): 1263 \text{ and } 746 \text{ cm}^{-1}. \begin{array}{l}
\begin{array}{c}
\text{1H-NMR (400 MHz, Chloroform-d, TMS/ppm)} \\
\delta \begin{array}{c}
(\text{Figure 4): 8.25-8.23} \\
\text{(d, J: 8.0 Hz, 4H), 8.01 7.99 (d, J: 8.0 Hz, 4H), 4.30 (t, J: 8.0 Hz, 8H), 1.77 (m, J: 8.0 Hz, 8H), 1.43 (m, J: 8.0 Hz, 8H), 1.34 (m-overlap, J:4.0 Hz, 16H), 0.89 ppm. (m, J:8.0 Hz, 12H).}
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\begin{array}{l}
\begin{array}{c}
\text{13C-NMR (100 MHz, Chloroform-d, TMS/ppm)} \\
\delta \begin{array}{c}
168.48, 133.01, 130.42, 130.38, 121.35, 65.62, 31.49, 28.53, 25.65, 22.54, 14.01 \text{ ppm. HRMS (Figure 6): (Molecular mass;764.4) Found: 764.4 M. The first temperature at which PTHE begins to degrade is 349 °C (TGA) (Figure 7).}
\end{array}
\end{array}
\end{array}

**Figure 3:** FTIR spectrum of PTHE.
Figure 4: $^1$H-NMR of PTHE.

Figure 5: $^{13}$C-NMR of PTHE.
2.3. Preparation and Characterization of wPMMA-PTHE Solution and Film

150 mg of wPMMA was added to a capped bottle, then 10 mL of toluene was added and stirred at 50 °C for 24 hours with a magnetic stirrer. A clear solution of wPMMA was obtained, and 1% by mass of PTHE was added to it. A homogeneous solution of wPMMA:PTHE was obtained by stirring for a further 2 hours.

100 mL of the wPMMA:PTHE toluene solution was dropped on a clean 2.5 x 2.5 cm glass tile, rotating at 2000 rpm. After this film dried, the process was repeated 10 times to build thickness, and the film was left to dry at room temperature. Pictures of the prepared transparent and green-emissive wPMMA:PTHE film under daylight and UV light are given in Figure 8.

The Fourier transform infrared (FTIR-ATR) characterization study of wPMMA:PTHE film, in comparison with PTHE and wPMMA, is given in Figure 9. Aromatic C-H peaks of PTHE are seen at 2951 cm⁻¹ and 2928 cm⁻¹. C=O, which belongs to ester bonds, exhibited strong peaks at 1726 cm⁻¹ and 1710 cm⁻¹. Additionally, a strong peak of C-O is observed at 1263 cm⁻¹ and is compatible with the literature (42). The aliphatic C-H peak of wPMMA shows itself weakly at 2949 cm⁻¹. C=O and C-O peaks belonging to the ester structure are seen as sharp and intense at 1724 cm⁻¹ and 1143 cm⁻¹, respectively. In the wPMMA:PTHE film, it has the characteristic peaks of the two materials. Due to the high PMMA ratio, wPMMA characteristic peaks are dominant. However, the presence of two new intense peaks observed at 796 cm⁻¹ and 1016 cm⁻¹ indicates that there is an interaction between the wPMMA and PTHE (Figure 9).

The X-ray diffractions (XRD) of PTHE powder, wPMMA, and wPMMA:PTHE are given in Figure 10. PTHE powder showed peaks at 2θ = 8.6, 10.76, 13.0, 15.36, 16.72, 17.56, 18.16, 18.44, 21.48 (intense), 23.8, 24.88, 25.56, 42.56 and 43.48. The values of the broad 2theta peaks of wPMMA and wPMMA:PTHE films are approximately 13.68 (intense), 25.0, and 42.56, respectively. It exhibited broadness, which is characteristic of wPMMA and belongs to the amorphous structure. In the wPMMA:PTHE film, 2theta peaks belonging to PTHE were not observed due to the low PTHE doping rate (Figure 10) (43).
3. RESULTS AND DISCUSSION

The absorption and photoluminescence spectra of PTHE in toluene [1x10^{-6} M] and in wPMMA (1 wt%) are given in Figure 11a. Dilute PTHE in toluene exhibits absorbance peaks at 474 and 445 nm belonging to the n-π* transitions associated with its extended aromatic π system (38,42). Compared to a previously reported study (41), the absorption of PTHE is almost the same as in chloroform solution (λ_{abs max}: 472 nm). For the preparation of solid films, 1 wt% doping of PTHE into wPMMA was chosen to control aggregation of the PTHE. In the wPMMA:PTHE film the absorption peaks (λ_{abs max}) of PTHE were found to be nearly identical to the toluene solution, at 472 and 443 nm.

In the PL spectrum of PTHE, it was found that the λ_{PL max} shifted from 492 to 525 nm on changing from solution to film measurements. PTHE is proposed to exhibit excimer behavior in wPMMA that gives rise to this wavelength shift, motivated by fact that there was no significant difference in the absorption spectrum (that might indicate ground-state aggregate formation) and that the PL spectrum exhibited only a single peak at longer wavelengths. Emission lifetime measurements of the solution and wPMMA:PTHE film were also performed, it was
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The longer wavelength excimer emission in the film phase also increases the Stokes shift compared to the monomeric behaviour in dilute solution (shifts of 772 and 2139 cm⁻¹), significantly reducing reabsorption of PTHE in the film phase. Indeed, the absolute PLQY (Φ) in the film is quite high, as in solution: 98 and 84% in solution and film, respectively (Table 1). Commission Internationale de l'éclairage (CIE) chromaticity coordinates of the PL spectra are shown in Figure 11c, with the excimer emission providing a slightly different emission colour point for the film. The PL\text{max} intensity of the film, which was exposed to the excitation wavelength at its maximum absorption in the kinetic mode of the Edinburgh FS5 fluorometer for 90 minutes, was measured at 525 nm every second and exhibited a highly photostable behavior (Figure 11d).

Table 1: Average lifetime value (τ) of wPTHE in toluene (1x10⁻⁶ M) and at film phase (%1 doped in wPTHE).

<table>
<thead>
<tr>
<th>PTHE</th>
<th>τ₁ (ns)</th>
<th>%</th>
<th>τ₂ (ns)</th>
<th>%</th>
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<tbody>
<tr>
<td>In toluene</td>
<td>3.80</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>In wPMMA</td>
<td>3.77</td>
<td>61.71</td>
<td>15.38</td>
<td>38.29</td>
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Figure 11: a) Absorption and PL spectra of PTHE in solution and film phase. b) Lifetime decay of PTHE in solution and wPMMA (%1 doped PTHE). c) CIE diagrams of PL spectra of PTHE in toluene (1x10⁻⁶ M) and in wPMMA. d) Optical stability test of PTHE.
4. CONCLUSION

The increasing use of plastics and the resulting serious environmental threat they pose must be addressed by all means available. In this study, solutions of waste PMMA were combined with an organic dye to produce green-emissive films suitable for photonics applications. Reprocessing such waste into high-value products may contribute to SDG goals and services within the scope of a sustainable future, clean energy, and energy efficiency (40).

PTHE, which is homogeneously dispersed in waste PMMA, absorbs blue light in the range of 400-500 nm when only 1% is added while also exhibiting a very high fluorescence quantum yield. Reusing waste PMMA with different combinations of fluorophores in this way could open the door to its use in many photonic technologies that absorb, transform, or emit wavelengths.

5. ACKNOWLEDGMENTS

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6. REFERENCES


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