Energy, Fuels and Chemicals

Catalytic Technologies for Waste Valorisation

Catalytic Degradation and Valorisation of Plastic Waste

KEYWORDS: Added-value materials/ Chemical vapour deposition (CVD)/ Carbon nanotubes (CNTs)/ Controlled Degradation of PLA

Plastic derived carbon nanotubes (CNTs) with different properties were prepared by chemical vapour deposition (CVD) using low-density polyethylene (LDPE) as carbon feedstock, thus providing a more sustainable alternative to the conventional use of pure hydrocarbons. Industrial-grade clays and ZnO were successfully used as catalysts to accelerate the hydrolysis of poly(lactic acid)(PLA) fibers under composting conditions.

Introduction

The world's plastics production has been increasing stiffly over the years, with recent estimates suggesting a cumulative plastic waste generation of over 25,000 million metric tonnes by 2050. Among these, 36.4% are expected to be discarded in landfills or in the environment; a similar fraction (36.4%) would be incinerated, and only 27.2% would be recycled. These forecasts clearly point out that plastic wastes are being mismanaged, mainly because current technologies are unable to promote proper reusing/recycling of these materials. Using plastic wastes as feedstock to produce added-value products and/or materials has been proposed as the boost needed to increase the attractiveness of plastics recycling. The conversion of plastic wastes into carbon materials is among such new approaches. Having that in mind, the main goal of this research topic is to prepare added-value carbon materials, such as carbon nanotubes (CNTs) and graphene-based materials, using plastic wastes as an alternative to the use of pure and costly gaseous carbon feedstocks (*e.g.*, methane, acetylene, and benzene).

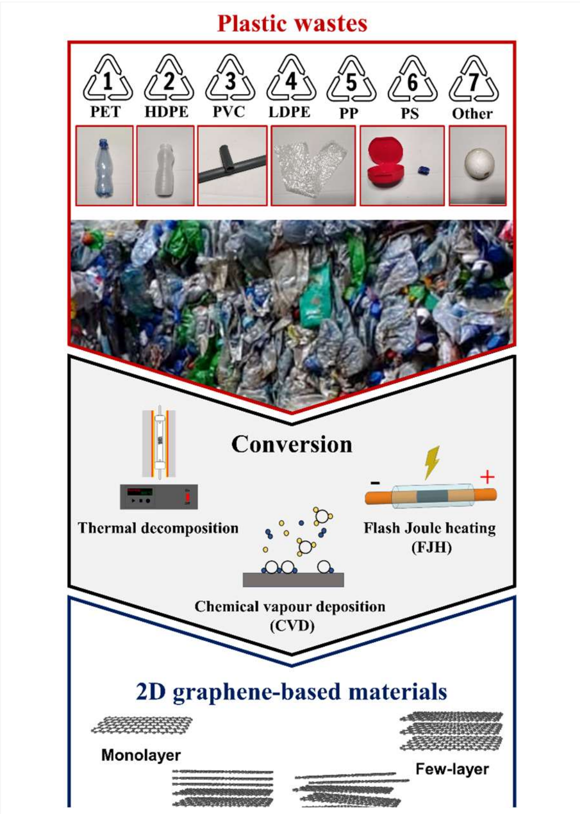

Fig. 1. Conversion of plastic wastes into valuable 2D graphene-based materials [2].

Replacing petrochemical-based plastics with biomass-derived materials can also contribute towards limiting plastic waste accumulation when proper waste management practices are not implemented. For example, polypropylene used to produce twines that support and manage crops in greenhouses can be replaced with biomass-derived and compostable PLA. As a result, at the end of the season, the green waste and the plastic residue can be degraded together, producing CO_2, water, and biomass substances. However, higher production costs and relatively slow degradation rates hinder the widespread application of PLA products [1]. Thus, in collaboration with our industrial partner, The Royal Lankhorst Euronete International group, we focused on developing commercially valid solutions to accelerate the hydrolytic degradation of PLA twines under composting conditions.

Current Development

The conversion of plastic wastes in added-value carbon materials has been studied under a collaboration with Prof. Helder T. Gomes (IPB – Polytechnic Institute of Bragança, Portugal) and the intermunicipal waste management company, "Resíduos do Nordeste, EIM", Portugal. A literature review was first conducted to assess the level of development in the field [2]. This study confirmed the current research trend towards the conversion of plastic wastes into valuable carbon materials. In addition to the classical carbonization of plastic wastes into activated carbons, the interest in synthesising valuable CNTs and graphene-based materials has been growing steadily over recent years (Fig 2).

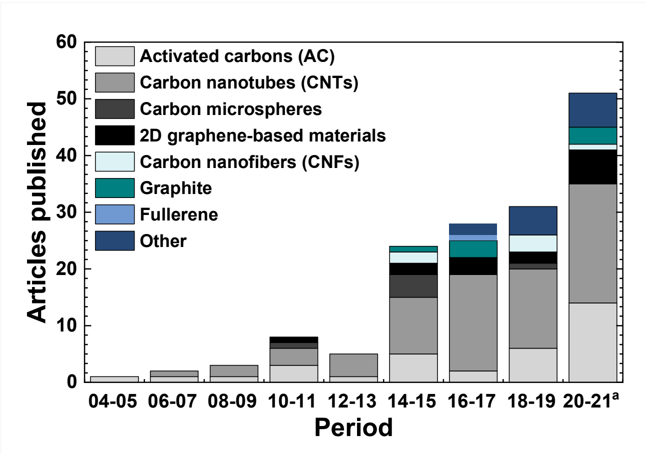

Fig. 2. Evolution of the Scopus's indexed original research articles dealing with conversion of plastics into carbon materials. a Data collected on June 29, 2021 [2].

In face of the above, we devoted our efforts into developing a methodology for the synthesis of CNTs through a chemical vapour deposition (CVD) method using LDPE as carbon feedstock [3]. Accordingly, four CVD catalysts were prepared by wetness impregnation and co-precipitation (using Al_2O_3, Ni, Fe and/or Al) and implemented to grow CNTs. The properties of the resulting CNTs were thoroughly characterized, including SEM, TEM, N_2 physisorption, thermogravimetric analysis, pH drift tests, and ICP-OES of the solution resulting from the acidic digestion of the CNTs. Hollow cavities were clearly observed in all the materials (Fig. 3) regardless of the catalyst employed in the CVD system, allowing to conclude that the proposed methodology is suitable for the synthesis of CNTs. Nevertheless, the morphology of the CNTs depends on the CVD catalyst (Fig. 3). Beside LDPE, high-density polyethylene (HDPE) and polypropylene (PP) were also employed as carbon source for the synthesis of CNTs (data not shown). The ability of all the synthesized CNTs for persulfate activation and degradation of organic micropollutants was then shown under Topic 4.2.1.2.

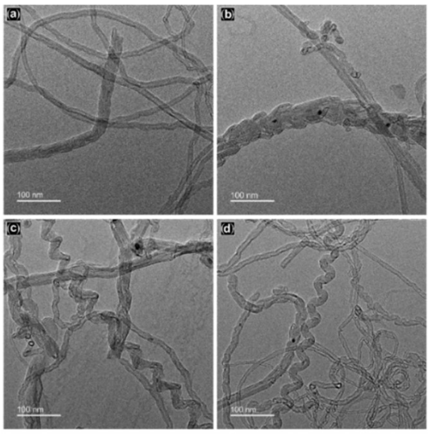

Fig. 3. Transmission electron microscopy (TEM) micrographs of the carbon nanotubes (CNTs) obtained by chemical vapour deposition (CVD) over different metal catalysts and using low-density polyethylene (LDPE) as carbon feedstock [3].

In collaboration with our industrial partner, The Royal Lankhorst Euronette, we were focused on selecting an appropriate catalyst to accelerate the hydrolysis of PLA, which is a primary depolymerization mechanism and the rate-controlling step of PLA biodegradation in compost. Considering that a suitable catalyst for hydrolytic degradation of PLA twines must combine high activity and thermal stability without compromising the properties of the PLA twine, materials with different textures and surface chemistry were blended in the PLA fibers [1]. The pristine PLA fibers and catalyst-containing samples were tested first by immersing them in water for extended periods (hydrolysis step), and later, selected samples were tested under composting conditions. The extent of the degradation of the PLA fibers was characterised using various techniques such as gel permeation chromatography (GPC), scanning electron microscopy (SEM), and thermogravimetric analysis. Among the catalysts studied, ZnO was found to be the most active catalyst for the hydrolytic degradation of PLA as shown in Fig. 4. Composting trials were conducted in collaboration with another industrial partner (Lipor, Portugal). Pristine PLA fibers and selected samples blended with catalysts were placed inside a real composting tunnel. Promising results were obtained with PLA fibers containing industrial-grade clays. The GPC measurements showed a 21% decrease in the PLA molecular weight after the composting.

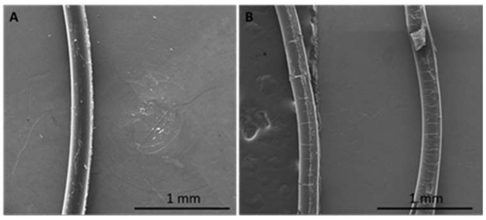

Fig. 4. Scanning electron microscopy (SEM) micrographs of (A) pristine PLA fiber and (B) PLA fiber with 1% ZnO, both after 240 h of hydrolysis [*].

Future Work

Biomass-derived liquid fuel is highly promising as sustainable replacement for fossil fuels. However, biomass contains a high content of oxygen and is hydrogen deficient, thus resulting in a low-grade liquid fuel with high acidity and viscosity, low heating value, and immiscibility with petroleum fuel. On the contrary, plastics (*e.g.*, polyethylene, polypropylene, and polystyrene) possess high carbon and hydrogen contents, but no oxygen. Therefore, an approach to be explored is to co-feed biomass with plastics during the production of biomass-derived liquid fuel. Increasing the economic attractiveness of plastic waste reusing/recycling (i) through the synthesis of added-value CNTs and (ii) to produce higher quality biomass-derived liquid fuels is expected to contribute towards reducing their input in the environment.

The knowledge transfer between FEUP and the R&D team from The Royal Lankhorst Euronette improved the understanding of the mechanism behind the controlled degradation of PLA under composting conditions. The company is actively searching for possibilities to commercialize products that take advantage of the developed solutions.

The project responded to several problems existing in the agriculture industry. For example, the growers' constant use of conventional PP twines poses a heavy environmental burden due to the lack of sustainable waste management processes that simultaneously degrade plastic and green residues. In addition, using PP twines in open-air crops leads to soil contamination via microplastic. These residues can enter the food chain and harm human life and health. These issues can be avoided using compostable PLA twines developed in this project.

In addition, the assessment of the available literature in the field of PLA highlighted the lack of a comprehensive review focused on the current state-of-the-art solutions for improvements in the degradation of PLA in technical applications. Thus, the collaboration resulted in a highly-cited review paper [1], awarded C—Journal of Carbon Research 2023 Best Paper Award" in 2023 by the journal's editorial board.

Related Sustainable Development Goals

Outputs

Master Dissertations

[*] F. Miranda, *Development of a catalyst for accelerated hydrolytic degradation of PLA greenhouse twines*, MIEQ, FEUP, 2018

S. Teixeira, *Catalyzed hydrolysis of PLA twines in composting conditions*, MIEQ, FEUP, 2019

L. Azevedo, *Carbon membranes for water treatment*, MIEA, FEUP, 2021

Selected Publications

[1] S. Teixeira *et al.*, C Journal of Carbon Research 7, 42 (2021).

[2] O. Vieira *et al.*, Chemical Engineering Journal 428, 131399 (2022)
[3] R.S. Ribeiro *et al.*, Journal of Environmental Management 308, 114622 (2022)

Team

Adrian M.T. Silva, Associate Professor; **José L. Figueiredo**, Emeritus Professor; **M. Fernando R. Pereira**, Full Professor/ Group Leader; **Katarzyna M. Eblagon**, Researcher (Doctorate Initial Level); **Lucília S. Ribeiro**, Researcher (Doctorate Initial Level); **Rui S. Ribeiro**, Researcher (Doctorate Initial Level); 3 masters students (theses above)

Funding

PLASTIC_TO_FUEL&MAT, POCI-01-0145-FEDER-031439, 2018-2022
LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023
LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
ALiCE, LA/P/0045/2020, 2021-2025
FCT Grants: 2022.04079.CEECIND
FCT Scholarship: SFRH/BD/143224/2019
K. Morawa Eblagon acknowledges funding from FCT under DL57/2016 Transitory Norm Programme