UNIVERSIDADE DA CORUÑA

IMPACT OF MECHANICAL RECYCLING ON ORGANIC ADDITIVES IN PLASTICS

E. Concha-Graña, C. Moscoso-Pérez, V. Fernández-González, P. López-Mahía, S. Muniategui-Lorenzo

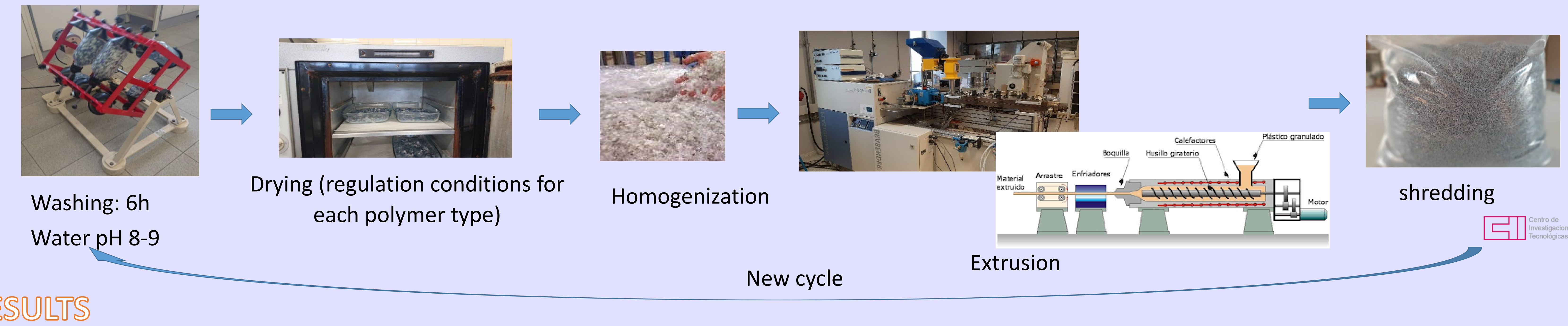
Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Universidade da Coruña, 15008 A Coruña, e.concha@udc.es

INTRODUCTION

The recycling of plastic provides a low-cost and environmentally friendly alternative for thermoplastics. Mechanical recycling is the most common approach (mainly used for PP, PE and PS). These processes can cause chemical changes in polymers or their additives. In this study, granules of three post-consumer polymers were subjected to several cycles of mechanical recycling, and changes in the content of organic additives were evaluated. Plastic organic additives (including 12 flame retardants, 6 UV filters, 5 antioxidants, 2 antimicrobials and 23 plasticizers) were quantitatively determined in the initial sample and in samples from 3 recycling cycles using ITEX-GC-MS/MS [1]. The qualitative analysis of non-target additives was performed by TD/Py-GC-MS.

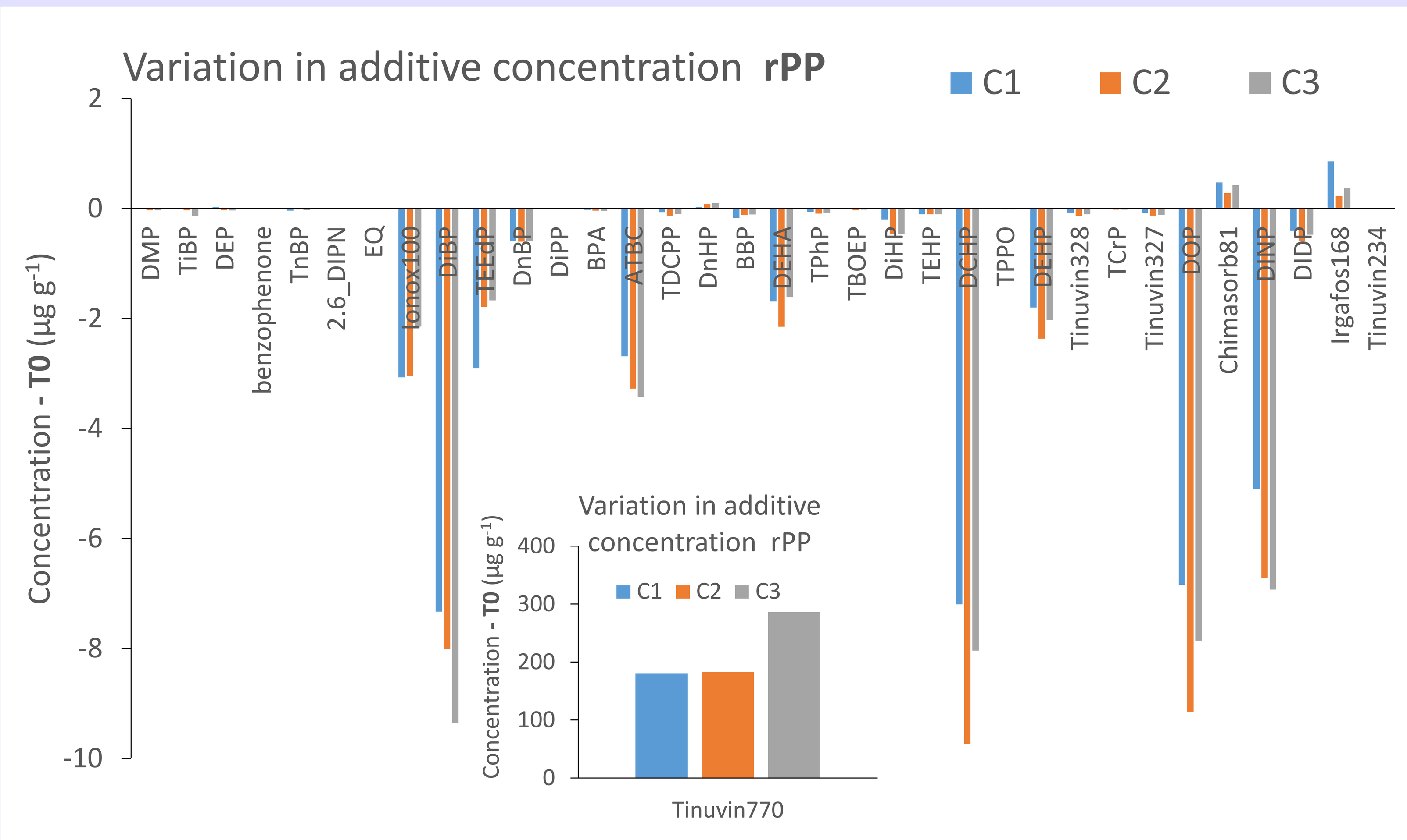
EXPERIMENTAL

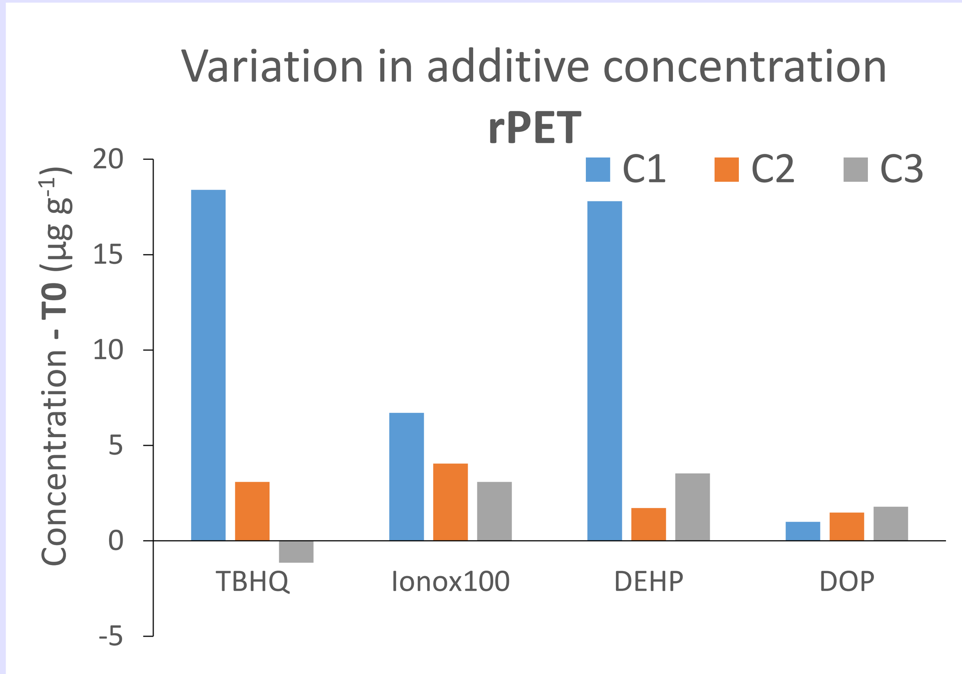
The selected post-consumer polymers (rPP, rPET, and rHDPE) were subjected to three consecutive mechanical recycling cycles, including washing, drying, extrusion, and shredding.

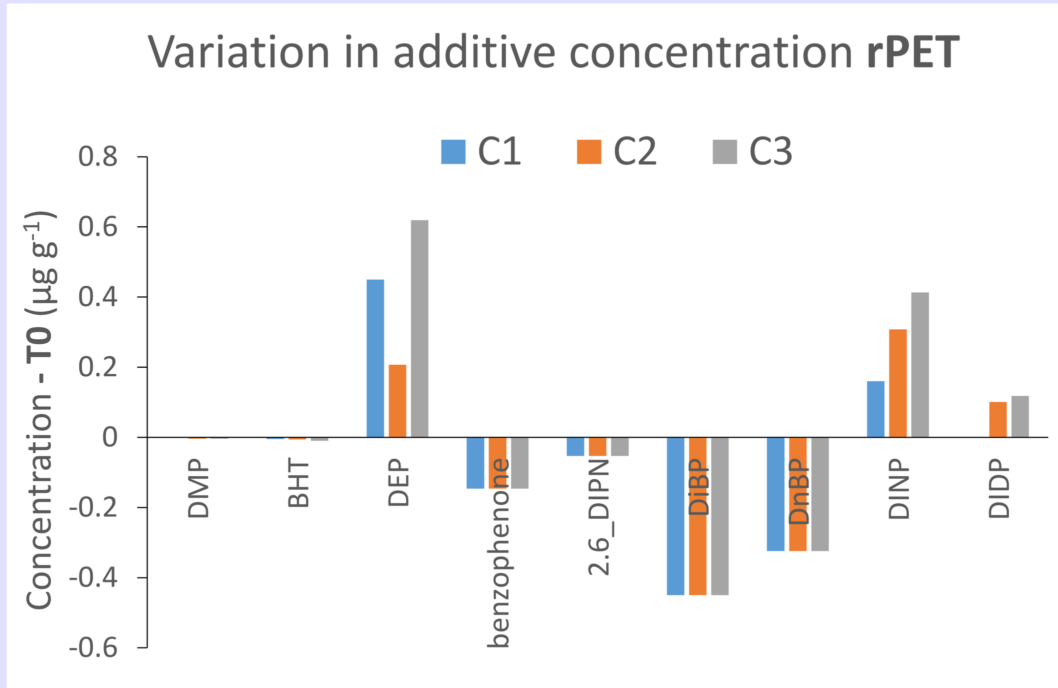


RESULTS

The quantitative analysis of additives showed different behaviors. For HDPE, almost no changes were detected in the concentration of additives. In the case of PP, recycling led to a reduction of about 50% in the total amount of additives.



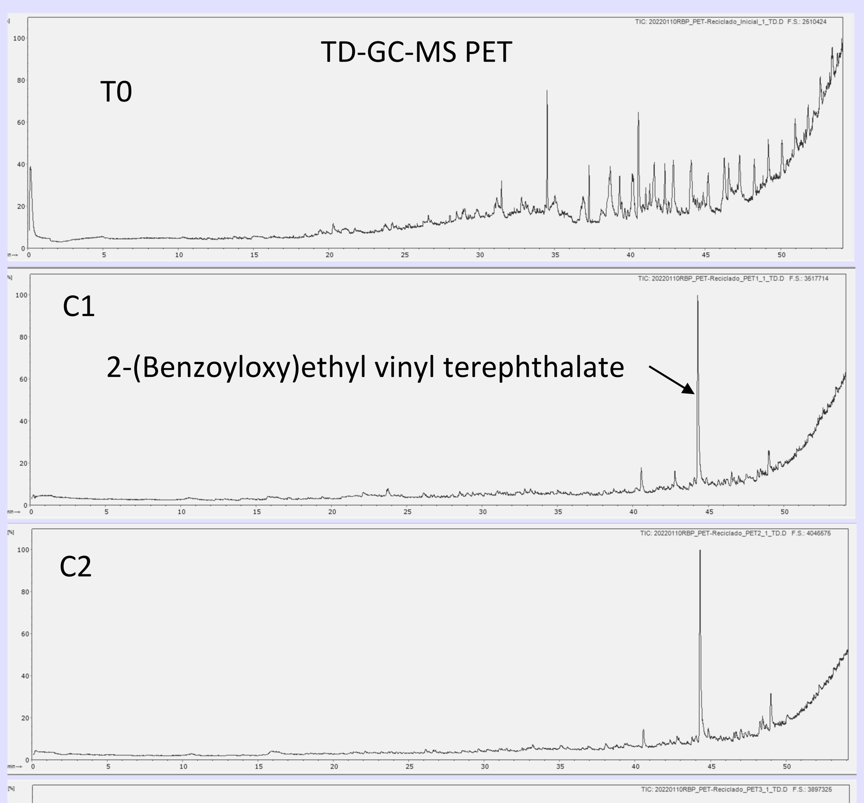




In the case of PET, an increase in the concentration of some phthalates, TBHQ and Ionox100 was observed in the first cycle, followed by a reduction in concentration in subsequent cycles.

The thermodesorption (TD/Py-GC-MS) screening analysis revealed changes in chromatographic profiles, primarily for PET and PP. In the case of PET, the appearance of a terephthalate after recycling stands out, which could indicate the degradation of the polymeric matrix. However, for this plastic, recycling mainly caused the loss or degradation of additives. For PP, some diene compounds appeared during the recycling process. Other compounds that were present in the initial polymer were not detected in the subsequent recycled samples.

Compounds detected in rPET	Initial	Cycle 1	Cycle 2	Cycle 3
Benzoic acid	✗	✓	✓	✓
1-Tridecene [CH2=CH(CH2)10CH3]	✓	✓	✗	✓
Divinyl terephthalate	✗	✓	✓	✓
Tridecene	✓	✗	✗	✗
1,3,5,7,9,11,13-Heptamethyl-1,13-tetradecadiene	✓	✗	✗	✗
Octadecamethylcyclononasiloxane	✓	✗	✗	✗
Eicosamethylcyclodecasiloxane	✓	✗	✗	✗
1-Hentriacontene [CH2=CH(CH2)28CH3]	✓	✗	✗	✗
Octacosamethylcyclotetradecasiloxane	✓	✗	✗	✗
Ethylene glycol dibenzoate	✗	✓	✓	✓
1-Dotriacontene [CH2=CH(CH2)29CH3]	✓	✗	✗	✗
2,4,6,8,10,12,14,16,18,20,22,24,26-Tridecamethyl-1,26-heptacosadiene	✓	✗	✗	✗
1-Hentriacontene	✓	✗	✗	✗
2-propenoic acid, 3-(4-methoxyphenyl)-, 2--ethylhexyl ester	✓	✓	✓	✓
1-Dotriacontene	✓	✗	✗	✗
Eruconitrile	✗	✓	✓	✓
1-Tritriacontene	✓	✗	✗	✗
1-Tetratriacontene	✓	✗	✗	✗
2-(Benzoyloxy)ethyl vinyl terephthalate	✗	✓	✓	✓
1-Pentatriacontene	✓	✗	✗	✗
1-Hexatriacontene	✓	✗	✗	✗
1-Heptatriacontene	✓	✗	✗	✗
1-Octatriacontene	✓	✗	✗	✗
2-(Benzoyloxy)ethyl biphenyl-4-carboxylate	✗	✓	✓	✓
Ethylene glycol bis(vinyl terephthalate)	✗	✓	✓	✓
1-Nonatriacontene	✓	✗	✗	✗



Compounds detected in rPP	Initial	Cycle 1	Cycle 2	Cycle 3
Tetrafluoroethylene	✓	✗	✗	✗
5-Methylfuran-2(3H)-one	✓	✓	✓	✓
n-Undecane [CH3(CH2)9CH7]	✓	✗	✗	✗
Decamethylcyclopentasiloxane	✓	✗	✗	✗
2,4,6,8-Tetramethyl-1-undecene (isotactic) (P-pentamer)	✓	✓	✓	✓
2,4,6,8-Tetramethyl-1-undecene (syndiotactic)	✓	✓	✓	✓
Tetradecamethylcycloheptasiloxane	✓	✗	✗	✗
2,4-Di-tert-butylphenol	✓	✓	✓	✓
2,4,6,8,10-Pentamethyl-1-tridecene (isotactic)	✓	✓	✓	✓
n-Nonadecane [CH3(CH2)17CH3]	✓	✓	✓	✓
2,4,6,8,10,12-Hexamethyl-1-pentadecene (isotactic)	✓	✓	✓	✓
2,4,6,8,10,12,14,16-Octamethyl-1,16-heptadecadiene	✗	✓	✓	✓
n-Eicosane [CH3(CH2)18CH3]	✓	✓	✓	✓
Docosamethylcycloundecasiloxane	✓	✗	✗	✗
n-Heneicosane [CH3(CH2)19CH3]	✓	✓	✓	✓
n-Docosane [CH3(CH2)20CH3]	✗	✓	✓	✓
2,4,6,8,10,12,14,16,18,20-Decamethyl-1,20-henicosadiene	✗	✓	✓	✓
n-Tricosane [CH3(CH2)21CH7]	✓	✓	✓	✓
1-Heptacosene [CH2=CH(CH2)24CH3]	✗	✓	✓	✓
n-Heptacosane [CH3(CH2)25CH3]	✗	✓	✓	✓
n-Nonacosane [CH3(CH2)27CH3]	✗	✓	✓	✓
2-(Benzoyloxy)ethyl vinyl terephthalate	✓	✗	✗	✗
2,4,6,8,10,12,14,16,18,20,22-Undecamethyl-1,22-tricosadiene (isotactic)	✗	✓	✓	✓
2-(Benzoyloxy)ethyl biphenyl-4-carboxylate	✓	✗	✗	✗
Ethylene glycol bis(vinyl terephthalate)	✓	✓	✓	✓
Pentadecamethyl-1,30-hentriacontadiene	✗	✓	✓	✓

CONCLUSIONS

Mechanical recycling involves only physic processes, and therefore, its effect on the chemicals in the plastic is limited, mainly affecting to the most volatile compounds or causing contamination contributions from recycling.

Other processes, such as chemical recycling (catalysis, hydrogenation or chemical depolymerisation) can potentially have a greater effect on additives. This process is typically used for PET recycling in combination with the mechanical recycling.

ACKNOWLEDGEMENTS

EU Funding for Research&Innovation (H2020-LABPLAS project, Ref. 101003954-H2020-SC5-2020-2). PID2022-138421OB-C21 financed by MICIU/AEI/10.13039/501100011033 cofinanced by FEDER, UE. Financial support is also acknowledged to the Program of Consolidation and Structuring of Units of Competitive Investigation of the University System of Galicia (Xunta de Galicia) potentially co-financed by ERDF (ED431C 2021/56).

[1] E. Concha-Graña, et al. Anal Chim Acta 1302 (2024) 342487. https://doi.org/10.1016/j.aca.2024.342487

23-27 SEPTEMBER 2024, LANZAROTE, SPAIN