Check for updates

BRIEF REPORT

Recovery and potential use for non-polyolefin materials after physical recycling of complex multilayers

[version 1; peer review: 2 approved with reservations]

Vanessa Gutiérrez[1], Miguel Mafé[2], Lucie Prins[3], Annemieke van de Runstraat[3]

[1]Mechanical Recycling, AIMPLAS - Plastic Technology Center, Paterna, Valencia, 46980, Spain
[2]Material Characterization & Testing Group, AIMPLAS-Plastic Technology Centre, Paterna, Valencia, 46980, Spain
[3]Sustainable Process & Energy Systems, TNO - Dutch Organization for Applied Scientific Research, Delf, 2628, The Netherlands

v1 **First published:** 27 Nov 2024, **4**:255
https://doi.org/10.12688/openreseurope.18912.1
Latest published: 27 Nov 2024, **4**:255
https://doi.org/10.12688/openreseurope.18912.1

Abstract

Standard flexible packaging in the market contains many components that differ from polyolefins (PO). These components can include barrier materials (Polyamides (PA), Polyethylene-terephthalate (PET), Ethylene-vinyl alcohol (EVOH), Polyvinyl-alcohol (PVOH), and aluminum), inks, lacquers, adhesives, fillers, and pigments. All these materials are insoluble in the solvents used for the physical, dissolution-based, and recycling of polyolefins, leaving them as a solid residue in the process. Characterization of the residue obtained after physical recycling of printed/metallized polyolefin flexible structures using the TNO Möbius dissolution process was performed to select potential applications, stakeholders, and/or secondary valorization routes. The residue resulted in a heterogeneous material composed of PET (60%), inorganic fraction (28%), and other organic components (12%). The potentially valuable materials from this residue are the PET and aluminum fractions. After a desk study, possible secondary recovery techniques for PET and aluminum were selected.

Plain language summary

Standard flexible packaging in the market contains many different materials (different types of plastics, aluminum, inks, lacquers, adhesives, fillers, and pigments). These materials can be used as water and oxygen protection and for structural and marketing purposes. All these materials are insoluble in the solvents used in the dissolution-based recycling of polyolefins (main components of flexible packaging), leaving them as a solid residue in the process. After a characterization of this residue, it was discovered that the main materials recovered have high market value and could be recovered for new applications.

Open Peer Review

Approval Status ? ?

	1	2
version 1 27 Nov 2024	? view	? view

1. **Dr. Zahid Iqbal Khan**, Universiti Teknologi Malaysia, Johor Bahru, Malaysia

2. **Giusy Santomasi**, Politecnico di Bari Dipartimento di Ingegneria Civile Ambientale del Territorio Edile e di Chimica (Ringgold ID: 124248), Bari, Italy

Any reports and responses or comments on the article can be found at the end of the article.

Keywords
Multilayer films, polyethylene-terephthalate, physical recycling, dissolution, polyolefins, metallized package.

This article is included in the Horizon 2020 gateway.

Corresponding author: Vanessa Gutiérrez (vgutierrez@aimplas.es)

Author roles: Gutiérrez V: Conceptualization, Investigation, Methodology, Resources, Validation, Visualization, Writing – Original Draft Preparation; **Mafé M**: Investigation, Methodology, Resources; **Prins L**: Investigation, Validation, Writing – Review & Editing; **van de Runstraat A**: Investigation, Validation, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

Grant information: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101003864 project name CIMPA (a circular multilayer plastic approach for value retention of end-of-life multilayer films)
The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Copyright: © 2024 Gutiérrez V *et al*. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

How to cite this article: Gutiérrez V, Mafé M, Prins L and van de Runstraat A. **Recovery and potential use for non-polyolefin materials after physical recycling of complex multilayers [version 1; peer review: 2 approved with reservations]** Open Research Europe 2024, **4**:255 https://doi.org/10.12688/openreseurope.18912.1

First published: 27 Nov 2024, **4**:255 https://doi.org/10.12688/openreseurope.18912.1

Introduction

In the packaging industry, a large majority of multi-material (multilayer) structures are used to achieve a high barrier against different factors, such as oxygen, water vapor, and CO_2, thus increasing the shelf life of packaged goods (e.g., food products). These structures have variable compositions, but are mainly based on polyolefin (PO): polyethylene or polypropylene. Polyolefins are laminated with different barrier materials, such as polyamide (PA), polyethylene-terephthalate (PET), ethylene-vinyl alcohol (EVOH), polyvinyl alcohol (PVOH), and aluminum; most structures also contain adhesives, labels, inks and pigments, fillers, lacquers, and other components, to ensure functionality and branding. All these materials hamper the mechanical recycling of PO, resulting in low-quality (downcycled) recyclates. To improve the recycling yield and quality of multilayer and multimaterial packages, novel recycling technologies, such as physical recycling (with the aid of solvents), are being implemented. One of these processes is the TNO Möbius dissolution process, developed by TNO.

In the TNO Möbius physical recycling process, PO is recovered from metallized multilayers using a solvent that selectively dissolves PO, whereas other non-PO components remain undissolved. This means that the other layers comprising metal, other polymers, and pigments remained intact and shrank somewhat. The undissolved residue was separated from the polymer solution using a coarse filtration step. The amount of recovered residue after the coarse filtration step varied depending on the composition of the waste, that is, the content of the non-PO material. Typically, 98% of non-PO material was recovered in this step. The polymer solution was further purified via a fine filtration step using a filtration aid. In this step, all the remaining fine particles, such as pigments and metals, were retained. The residue was then dried and weighed.

This work presents the characterization of the recovered residue and the possibilities for secondary recovery of the potentially valuable materials contained therein.

Methods

The residue collected from the PO physical recycling process of metallized packaging waste was treated and tested according to the following methods: Fourier Transform Infrared Spectrophotometry (FT-IR), Differential Scanning Calorimetry (DSC) Thermogravimetric analysis (TGA) and Thermogravimetric analysis (TGA). A preliminary evaluation was performed on five randomly selected flakes using FT-IR to verify the composition of the residue, followed by a homogenization step and a full characterization of the material.

Homogenization of the residue

The residue was micronized to obtain a homogeneous powder. The process was performed in a laboratory cutting mill SM 300 (Retsch) with a particle size of less than 1 mm. To prevent melting/sticking during micronization, the samples were frozen in liquid nitrogen.

Characterization of the residue

Residue was analysed according to the following laboratory techniques:

- Fourier-transform infrared spectrophotometry (FT-IR) was performed to verify the composition of the residue. A Perkin Elmer Frontier Spectrophotometer was used, and the measurement method was attenuated total reflection (ATR) on GLADIATR with diamond crystal, with a resolution of 4 cm-1, and a scan range of 4000 to 400 cm-1.
- Differential Scanning Calorimetry (DSC) analysis was performed on the residue using a POLYMA 214 calorimeter, according to standard UNE-EN ISO 11357, with the following heating program: 1st heating rate of 0 °C to 300ºC at 20ºC/min; Isothermal for 5 min at 300 °C; cooling rate of 300ºC to 0ºC at 20ºC/min; 2nd Heating rate of 0 °C to 300ºC at 20ºC/min.
- Thermogravimetric analysis (TGA) was performed on the residue in a QIR5000 TA INSTRUMENTS thermogravimeter, under air conditions, with a temperature range of 40ºC–600ºC.

Results and discussion

This residue consists of a mixture of non-PO materials present in flexible packaging, such as barriers, adhesives, inks, coating lacquers, and metallization. The material was heterogeneous with fluffy flakes (see Figure 1).

Preliminary evaluation

The following results, shown in Figure 2, were obtained from the preliminary characterization of individual flakes.

The summary of the composition of each flake is the following:

- For flakes #1 and #2, the FTIR spectra show characteristic bands of polyethylene terephthalate (PET) and bands that can be associated with calcium carbonate.
- The FTIR spectrum of flake #3 showed bands characteristic of polyethylene terephthalate (PET).
- Finally, for flakes #4 and #5, the FTIR spectra showed bands characteristic of ethylene-vinyl alcohol (EVOH).



Figure 1. Left: Pre-treated metallized waste. Right: Residue collected from the Möbius process at TNO. Scale in millimetres.

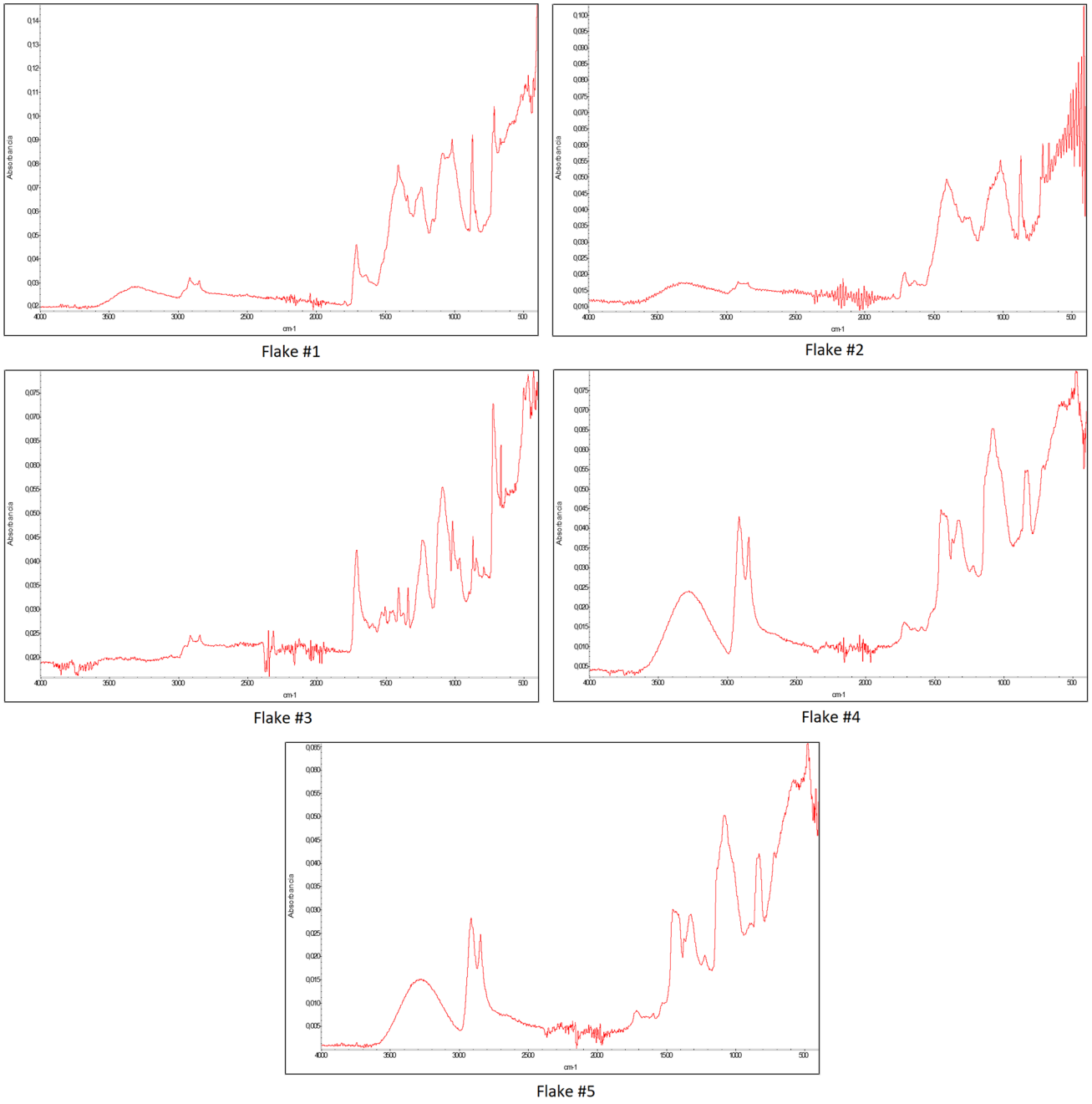

Figure 2. Fourier Transform Infrared Spectrophotometry (FT-IR) spectra form individual flakes tested.

The results obtained in this preliminary evaluation demonstrate the heterogeneity of the residue, which depends on the respective packaging foil from which it was recovered.

Homogenization

To obtain a more general impression of the main composition of the residue obtained from the physical recycling process, a micronization process was performed to obtain a homogeneous powder (Figure 3).

Characterization of the residue

The micronized residue was tested again by FTIR using the same methodology as in previous tests. Three samples of the micronized residue were collected randomly and tested, and the results are shown in Figure 4.

The FTIR spectra of the three samples from the micronized residue showed the characteristic bands of polyethylene terephthalate (PET) and polyurethane (PU). Other polymers,



Figure 3. Homogenized residue. Scale in millimetres.

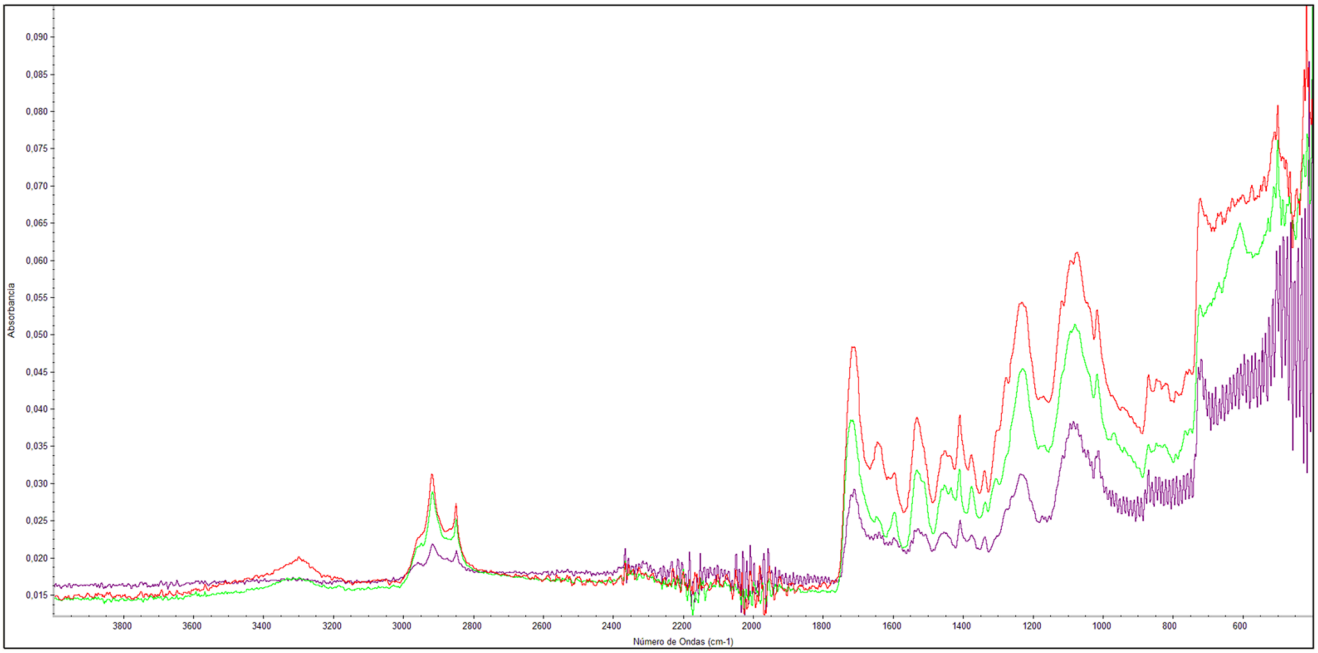

Figure 4. Fourier Transform Infrared Spectrophotometry (FT-IR) spectra form micronized residue.

such as EVOH, detected in the previous analysis, could be masked by the spectrum bands from the previously identified materials. These results are in line with previously identified flakes, showing the majority of PET in the residue.

To verify the presence of other polymers, Differential Scanning Calorimetry analysis was performed on a randomly collected sample from the homogenized residue. The results of the second heating cycle are shown in Figure 5.

The following transitions are identified from the above thermogram:

- Glass Transition – 78.5ºC (associated to PET).
- Melting point 1 – 124.8ºC (associated with LDPE/LLDPE) – enthalpy: 0.6038 J/g.
- Melting point 2 – 160.8ºC (associated with PP) – enthalpy: 0.8054 J/g.
- Melting point 3 – 243.6 ºC (associated with PET) Enthalpy: 15.97 J/g.

According to the enthalpies from each identified transition, the PO fractions (LDPE and PP) were present in very small amounts (residual from the dissolution process), indicating that PET was the major component. Transitions corresponding to EVOH, PA, or other polymers were not identified or were below the detection limit of the test. Thus, these transitions can also be masked.

The presence of other possible components in the residue was verified by thermogravimetric analysis (TGA). The thermograph and key weight losses are shown in Figure 6.

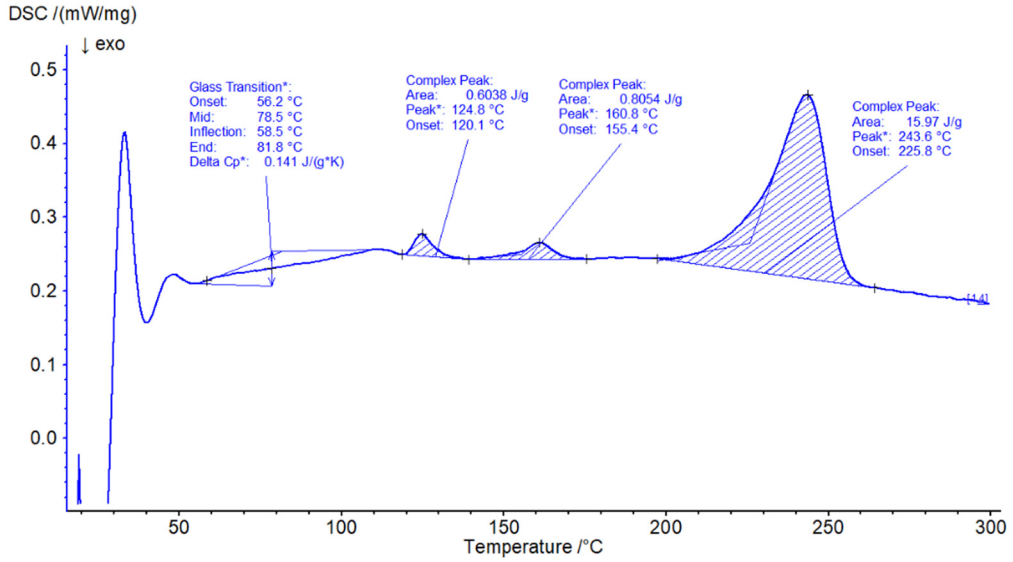

Figure 5. **Second heating rate thermogram of micronized residue sample.**

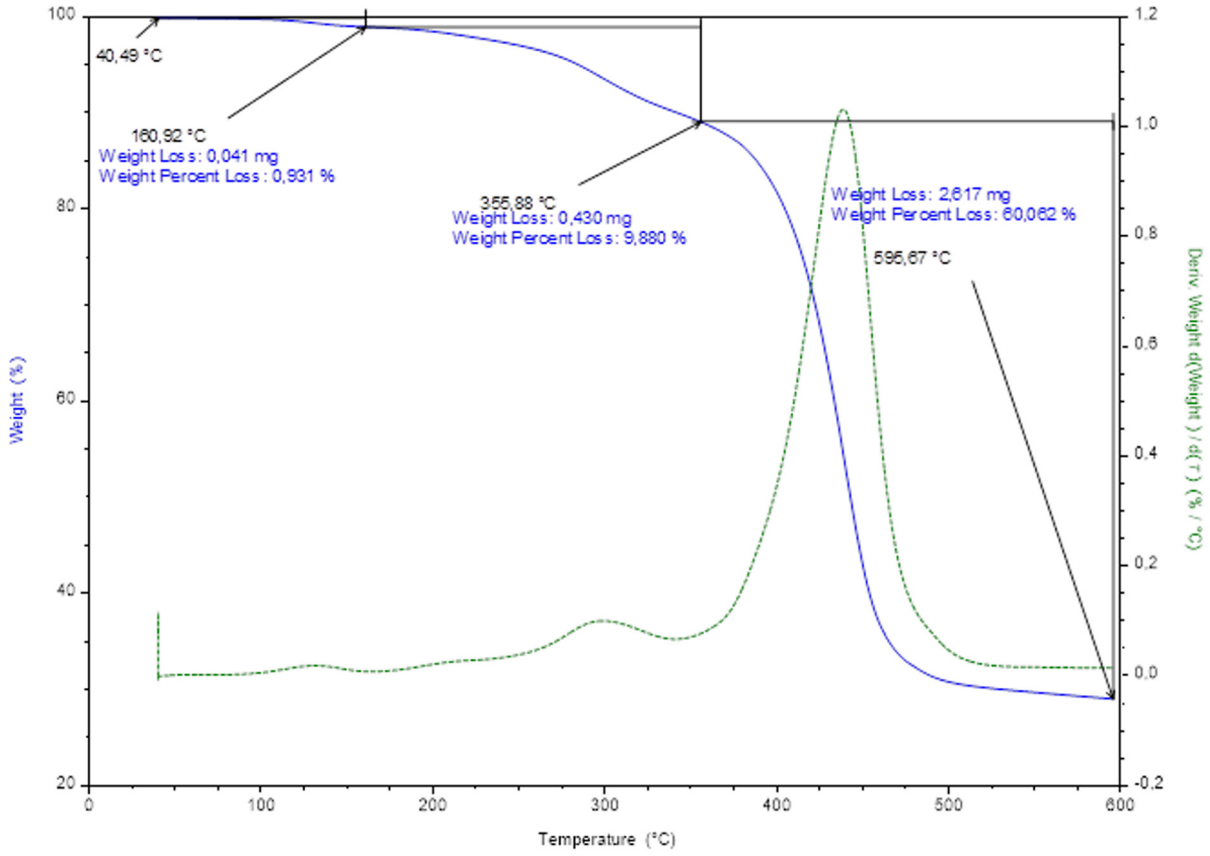

Figure 6. **Thermogravimetric analysis (TGA) of the micronized residue.**

The main weight losses detected in the TGA analysis are listed in Table 1. A possible correspondence to each loss is also noted in the table.

The results in Table 1 confirm once more the majority of PET components, reaching 60% of the composition of the residue, followed by the inorganic fraction (29%), which, in principle,

Table 1. TGA weight losses detected and possible correspondence.

Temperature range (ºC)	Weight loss (%)	Possible correspondence
40.49 to 160.92	0.931	Residual solvents, organic inks and pigments, lacquers
160.92 to 355.88	9.880	Adhesives, EVOH
355.88 to 595.67	60.062	PET
595.67	29.030	Aluminium, inorganic inks and pigments

is composed of aluminum, together with inorganic pigments, fillers, and other non-polymeric materials.

Owing to the composition of the residue and the high content of the inorganic fraction, its direct use could not be expected. For this reason, a secondary recovery is proposed to isolate and use the main components detected with potentially high market value: PET and aluminum.

The testing data related to the presented graphics (FTIR, TGA and DCS) is collected in the Underlying Data[1]

Secondary recovery options

Considering the existing industrialized process, from an economic point of view, PET chemolysis via hydrolysis and methanolysis are very capital-intensive processes; hence, they are not economically viable for small-scale production, and the residue must be mixed with other existing PET waste streams to reach a suitable scale. However, this is not the case for PET chemolysis via glycolysis, which may be economically viable for small- and medium-scale production[2–5].

According to the composition of the residue obtained after physical recycling of the PO waste (ca. 60% PET), the better choices of treatment are glycolysis and alkaline hydrolysis, due to the lower sensitivity to contaminants, together with the possible availability of stakeholders for direct treatment.

Alternative pyrolysis or gasification processes can be used, in which plastic mixtures are heated with air or oxygen to obtain synthesis gases, liquid residue (called pyrolytic oil), and separation and recovery of the inorganic fraction, such as metals, fillers, and fibers.

Although PET cannot be recovered during these processes, it is converted into other valuable materials, and Al can be collected from the solid fraction after pyrolysis. From this process, it has been reported that aluminum with a purity of 95.80% can be recovered from aluminized plastic packages such as flexible packages and TetraPAK containers[6,7]. At the industrial level, pyrolysis is already being used to recover aluminum from metallized plastic waste, which is an interesting option to recycle the residue.

Conclusions

Physical recycling of metallized flexible PO structures using TNO Möbius dissolution technology for recovering PO leaves a residue. Characterization of this residue was performed to select the potential applications, stakeholders, and/or secondary valorization routes. The residue was found to be a heterogeneous material composed of PET (60%), inorganic fraction (28%), and other organic components (12%). The potentially valuable materials from this residue are the PET and aluminum fractions. After a desk study, considering the possible secondary recovery techniques for PET and aluminum, the following technologies were selected as the most promising:

1. First, chemical recycling is used to recover the PET fraction, especially alkaline hydrolysis and glycolysis, owing to the low interference of the contaminants in the process, industrially available technologies, and the existence of potential stakeholders.
2. Second, pyrolysis is used to recover the aluminum fraction, turning PET and other components into oil and char for other chemical applications. For this process, there is also the potential application of the residue as a direct input for a stakeholder's plant.

A combination of the above could also be implemented with other technology, e.g., the "new" residue obtained from the chemical recycling process can be fed to a pyrolysis plant to recover the aluminum fraction.

Ethics and consent

Ethics and consent are not required for this study

Data availability statement

Underlying data

Zenodo: Recovery and potential use of non-polyolefin materials after physical recycling of complex multilayers: underlying data (https://doi.org/10.5281/zenodo.13767836)[1]

This project contains the following underlying data:

- FT-IR spectra. (Report FT-IR analysis of residue)
- DSC. (Report Thermogram of micronized residue sample).
- TGA curve. Report Thermogravimetric analysis of micronized residue sample)

Data are available under the terms of the Creative Commons Zero "No rights reserved' data waiver (CC0 1.0 Public domain dedication).

Author roles

Gutierrez V: Conceptualization, Investigation, Methodology, Visualization, Writing – Original Draft Preparation, Writing – Review & Editing; **Mafé M**: Investigation, Methodology; **Prins L**: Investigation, Methodology, Visualization, Writing – Review & Editing; **Runstraat A**: Investigation, Methodology, Writing – Review, & Editing.

References

1. Gutierrez V: **Recovery and potential use for non-polyolefin materials after physical recycling of complex multilayers - Underlying data**. *Zenodo.* [Dataset], 2024.
http://www.doi.org/10.5281/zenodo.13767836
2. Shojaei B, Abtahi M, Najafi M: **Chemical recycling of PET: a stepping-stone toward sustainability.** *Polym Adv Technol.* 2020; **31**(12): 2912–2938.
Publisher Full Text
3. Oku A, Hu LC, Yamada E: **Alkali decomposition of poly(ethylene terephthalate) with sodium hydroxide in nonaqueous ethylene glycol: a study on recycling of Terephthalic acid and ethylene glycol.** *J Appl Polym Sci.* 1997; **63**(5): 595–601.
Publisher Full Text
4. Siddiqui MN, Achilias DS, Redhwi HH, *et al.*: **Hydrolytic depolymerization of PET in a microwave reactor.** *Macromol Mater Eng.* 2010; **295**(6): 575–584.
Publisher Full Text
5. Sheel A, Pant D: **Chemical depolymerization of PET bottles via glycolysis**. *Recycling of polyethylene terephthalate bottles.* William Andrew Publishing, 2019: 61–84.
Publisher Full Text
6. Irawan C, Jelita R, Nata, FI: **Recovery of aluminum from aluminum coated plastic waste using pyrolysis process.** *Reaktor.* 2018; **18**(1): 38–44.
Publisher Full Text
7. Muñoz-Batista MJ, Blázquez G, Franco JF, *et al.*: **Recovery, separation and production of fuel, plastic and aluminum from the Tetra PAK waste to hydrothermal and pyrolysis processes.** *Waste Manag.* 2022; **137**: 179–189.
PubMed Abstract | **Publisher Full Text**

Open Peer Review

Current Peer Review Status: ? ?

Version 1

Reviewer Report 20 December 2024

https://doi.org/10.21956/openreseurope.20463.r47643

© **2024 Santomasi G.** This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

?

Giusy Santomasi
DICATECh, Politecnico di Bari Dipartimento di Ingegneria Civile Ambientale del Territorio Edile e di Chimica (Ringgold ID: 124248), Bari, Apulia, Italy

The article aimed to characterise and find secondary recovery pathways for non-polyolefin materials derived from the application of the TNO Möbius process. Characterisation was carried out using appropriate methodologies such as FTIR (Fourier transform infrared spectrophotometry), DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis). The resulting process residue consists of a heterogeneous mixture of PET (polyethylene terephthalate), aluminium and other components. Potential recovery routes are identified in chemical recycling and pyrolysis. This is a well-written article with interesting results that deserve to be published. However, there are several points that need to be clarified and improved.
In particular, the literature cited is inherent but not sufficient, the part concerning the obtained results needs to be supplemented with references. Particularly in the discussion of secondary recovery options, details must be added as to what is technically and economically feasible.
The reproducibility of the methods is ensured by the underlying data, however I would add references, where possible, also in the methods section to allow for more in-depth details on the methodology.

The conclusions need to be improved. I would suggest being more explicit in specifying the novelty of the work, highlighting the progress compared to the most recent state of the art of similar studies. What are the consequences and influence of this study on the recovery possibilities of flexible packaging complex multilayers.

References

1. Dogu O, Pelucchi M, Van de Vijver R, Van Steenberge P, et al.: The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy and Combustion Science*. 2021; **84**. Publisher Full Text

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Waste Management, Plastic waste mechanical recycling

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 03 December 2024

https://doi.org/10.21956/openreseurope.20463.r47638

© 2024 Khan D. This is an open access peer review report distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

?

Dr. Zahid Iqbal Khan
Universiti Teknologi Malaysia, Johor Bahru, Skudai, Malaysia

Summary of the Article
The article focuses on the characterization and potential secondary recovery of non-polyolefin (non-PO) materials derived from the TNO Möbius dissolution process. This process physically recycles polyolefins (PO) from complex, multilayered packaging structures, leaving a heterogeneous residue comprising polyethylene terephthalate (PET), aluminum, and other components. Key techniques like Fourier-transform infrared spectrophotometry (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were utilized to analyze the residue. The study proposes chemical recycling (via glycolysis or alkaline hydrolysis) and pyrolysis as potential recovery methods for PET and aluminum.
Evaluation and Expanded Answers
1. Is the work clearly and accurately presented and does it cite the current literature?
   - Answer: Partly.

- Details:
  - While the article is generally well-written, some sections lack clarity in presenting complex concepts. For instance, the methodology descriptions are not comprehensive enough to fully understand the processes used.
  - Current literature is cited, but its integration into the discussion is inconsistent. Some key claims, such as the economic feasibility of glycolysis, lack sufficient supporting references.
  - To address this, the authors should provide more explicit citations and explanations linking their results to previously published findings.

2. Is the study design appropriate and does the work have academic merit?
   - Answer: Yes.
   - Details:
     - The study design is sound and aligns with the goal of exploring secondary recovery options for non-PO materials. The choice of analytical techniques and the focus on a novel recycling process make this work academically valuable.
3. Are sufficient details of methods and analysis provided to allow replication by others?
   - Answer: Partly.
   - Details:
     - The methodologies for FTIR, DSC, and TGA analyses lack specific details (e.g., exact parameters for each step, sample preparation methods).
     - For full replication, the authors should include:
       - Detailed descriptions of sample preparation steps.
       - A clear explanation of how the homogenization process was standardized.
       - Specific parameters and calibration details for the equipment used.
4. If applicable, is the statistical analysis and its interpretation appropriate?
   - Answer: Not applicable.
5. Are all the source data underlying the results available to ensure full reproducibility?
   - Answer: Yes.
   - Details:
     - The source data, including FTIR spectra, DSC thermograms, and TGA curves, are accessible via Zenodo, ensuring reproducibility.
6. Are the conclusions drawn adequately supported by the results?
   - Answer: Partly.
   - Details:
     - While the conclusions are generally consistent with the results, they are somewhat broad and lack quantitative analysis of economic and environmental impacts.
     - To strengthen the conclusions, the authors should:
       - Include quantitative comparisons of different recovery methods (e.g., cost analysis of glycolysis vs. pyrolysis).
       - Provide more detailed insights into the industrial scalability and environmental implications of their proposed recovery strategies.

Key Points to Address

1. Expand Methodological Details:
   - Ensure every analytical technique and step is described comprehensively to allow replication.
2. Enhance Literature Integration:

- Strengthen the discussion by better integrating cited literature and providing references to support critical claims.

3. Quantify Economic and Environmental Aspects:
   - Include cost-benefit analyses and environmental impact assessments of the proposed recovery methods.
4. Improve Results Presentation:
   - Enhance figure annotations for easier interpretation.
   - Discuss the implications of spectra masking in FTIR and DSC results.
5. Conclude with Specificity:
   - Refine the conclusions to directly address how the findings advance the field and their practical applications.

The article presents an interesting and relevant study, addressing the identified shortcomings will improve its clarity, scientific rigor, and utility. The recommended changes are necessary to ensure the article is both scientifically sound and practically valuable.

References

1. Khan Z, Habib U, Mohamad Z, Tufail A, et al.: Innovative hybrid nanocomposites of recycled polyethylene terephthalate/polyamide 11 reinforced with sepiolite and graphene nanoplatelets. *Journal of Thermoplastic Composite Materials*. 2024. Publisher Full Text
2. Muñoz-Batista MJ, Blázquez G, Franco JF, Calero M, et al.: Recovery, separation and production of fuel, plastic and aluminum from the Tetra PAK waste to hydrothermal and pyrolysis processes. *Waste Manag*. 2022; **137**: 179-189 PubMed Abstract | Publisher Full Text

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Dr. Zahid Iqbal Khan's research areas align closely with the themes of this article and include polymer recycling, sustainable material development, and hybrid nanocomposites. He specializes in the recycling and valorization of polyethylene terephthalate

(rPET) and other polymeric waste materials, with a focus on enhancing their mechanical, thermal, and rheological properties through the integration of advanced fillers like graphene nanoplatelets and sepiolite. His work emphasizes circular economy strategies, waste management, and environmental impact reduction by developing materials and processes for sustainable packaging and high-performance applications. Dr. Khan is also experienced in utilizing advanced analytical techniques such as FTIR, DSC, and TGA for material characterization, making him well-suited to evaluate research on recycling methodologies and their potential industrial scalability.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.