The Analysis of the Polyethylene Terephthalate Recycling Methods Using Plastic Degrading Enzymes

https://polychem-usa.com/pet-plastic-products/

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Introduction

Plastics

- Derived from Organic Material (How plastics)
  - Cellulose
  - Coal
  - Petroleum
  - Salt
  - Crude oil

Plastic bottle manufacturers address flexibility, sustainability ...

Introduction

Plastics

- First created in 1900s (Plastics-Chemistry)
- Increasing Popularity in use (Plastics-Chemistry)
  - Packaging
  - Fabric
  - Low production cost
- Plastics -classified as synthetic organic polymers (Plastics-Chemistry)

https://dissolve.com/video/Plastic-water-bottles-moving-through-bottle-manufacturing-royalty-free-stock-video-footage/001-D1117-67-03

Introduction

Recyling Plastic

- 3 Main Methods of Waste Disposal (Webb et al. 2012)
    - Burying in a landfill
    - Incineration
    - Recycling

https://www.mirror.co.uk/science/humans-produced-8-billion-tonnes-10885802

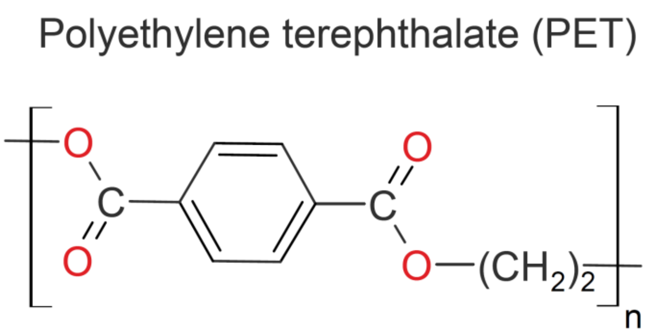
https://www.climatecentral.org/news/where-trash-is-a-burning-problem-17973

https://www.greenmatters.com/p/plastic-recycling

Introduction

Polyethylene Terephthalate (PET)

- Thermoplastic polyester (Shen, L. et al.)
  - Strong
  - Durable
  - Chemically stable
- Properties of PETs -most used material in a wide range of applications (Shen, L. et al.)
  - Additives extend life of products (Shen, L. et al.)
  - Worldwide plastic consumption (Shen, L. et al.)



http://polymerdatabase.com/Polymer%20Brands/PET.html

Introduction

Polyethylene Terephthalate (PET)

- Used for (Kawai et al. 2019)
  - Synthetic fabric
  - Packaging
    - Disposable water bottles
    - Soft drink containers
    - Sports equipment

http://www.clearpak.com/site/clear-plastic-packaging-materials/pet-polyethylene-terethphalate-plastic

Introduction

Enzymatic Degradation

- PET - insoluble due to **large size** of the polymer molecules (Kawai et al. 2019)
- Use of enzyme to depolymerize molecular structure (Kawai et al. 2019)
  - Water Soluble
- 2 Common Categories (Kawai et al. 2019)
  - Enzymatic surface modification of polyester fibers
  - Management of PET waste by enzymatic hydrolysis

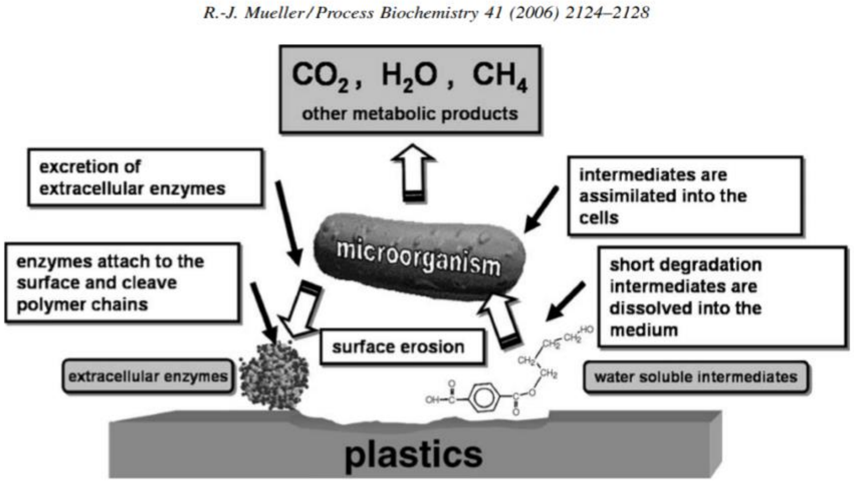


Fig. 1. Scheme of general mechanism of enzymatic catalyzed hydrolytic polymer degradation.

Introduction

Enzymatic Surface Modification of Polyester Fibers

- Plastic -exceptionally hydrophobic polymer (Vertommen, M. et al.)
  - Causes synthetic materials to be non-biodegradable
    - Major limitation – inability to break down plastics
      - Plastic enters landfills for hundreds of years

- Investigations involving enzymatic surface modification (Vertommen, M. et al.)
  - Technique uses enzymes to break down plastics at surface
  - Allows water to penetrate surface of plastic
  - Decreased time of plastic degradation

Literature Review

Schrader et al. (2006)

Purpose:

- Investigated a new thermophilic hydrolase enzyme from Thermobifida fusca (TfH)
- Isolated and expressed in E. coli

Results:

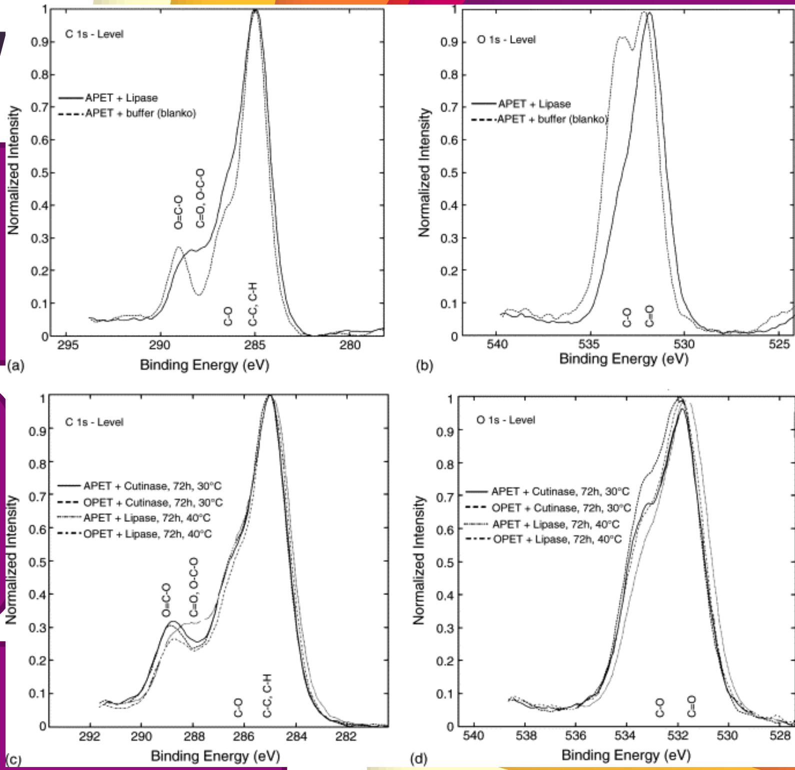
- Increased enzymatic degradation in polyesters containing aromatic constituents
- Ability to degrade commercial PET (beverage bottles)

Literature Review

Vertommen et al. (2004)

Purpose:

- Investigated enzymatic surface degradation in order to make PET recycling more efficient

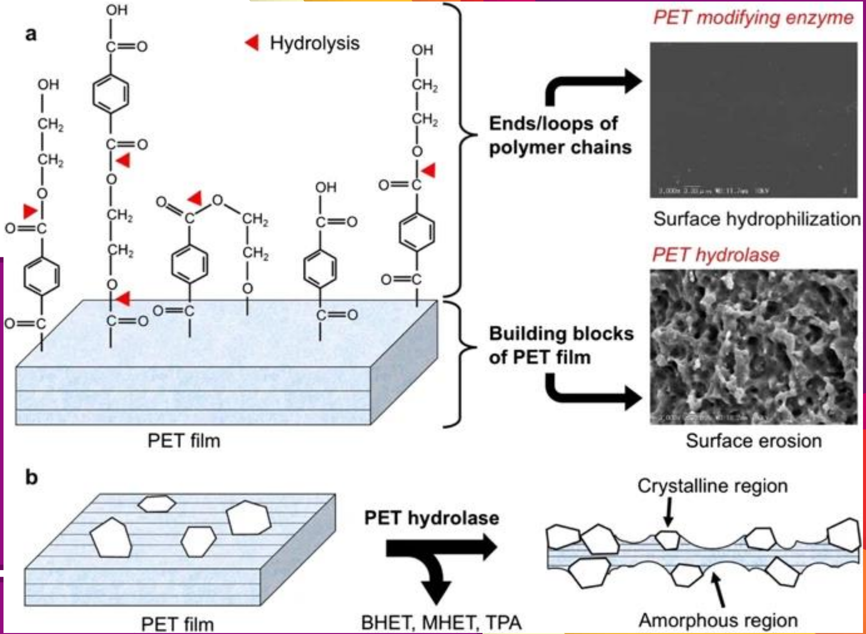


Results:

- In contrast to other research, no hydrolysis products were detected after treatment of crystalline or amorphous PET with this enzyme.
- Cutinase from *F. solani pisi* displays significant hydrolytic activity towards amorphous regions of PET

Literature Review

Kawai et al. (2019)



Purpose:

- Reviewed variety of journal articles
- Focused on PET hydrolases enzymes
  - -Enzymatic requirements for PET hydrolysis
  - -Structural analyses of PET hydrolases
  - -Reaction mechanisms

Results:

- Polyesterases broad substrate specificities –more applications
- PET hydrolases -applied for functionalization of general polyesters in addition to PET without damaging bulk properties of polyesters
- May be useful for forming complex structure with chemicals

Gap in the Research

PET Hydrolases and Hydrolysis of PET

- Understand properties of PET materials
- Structures of PET hydrolases-
- Enzymatic kinetics

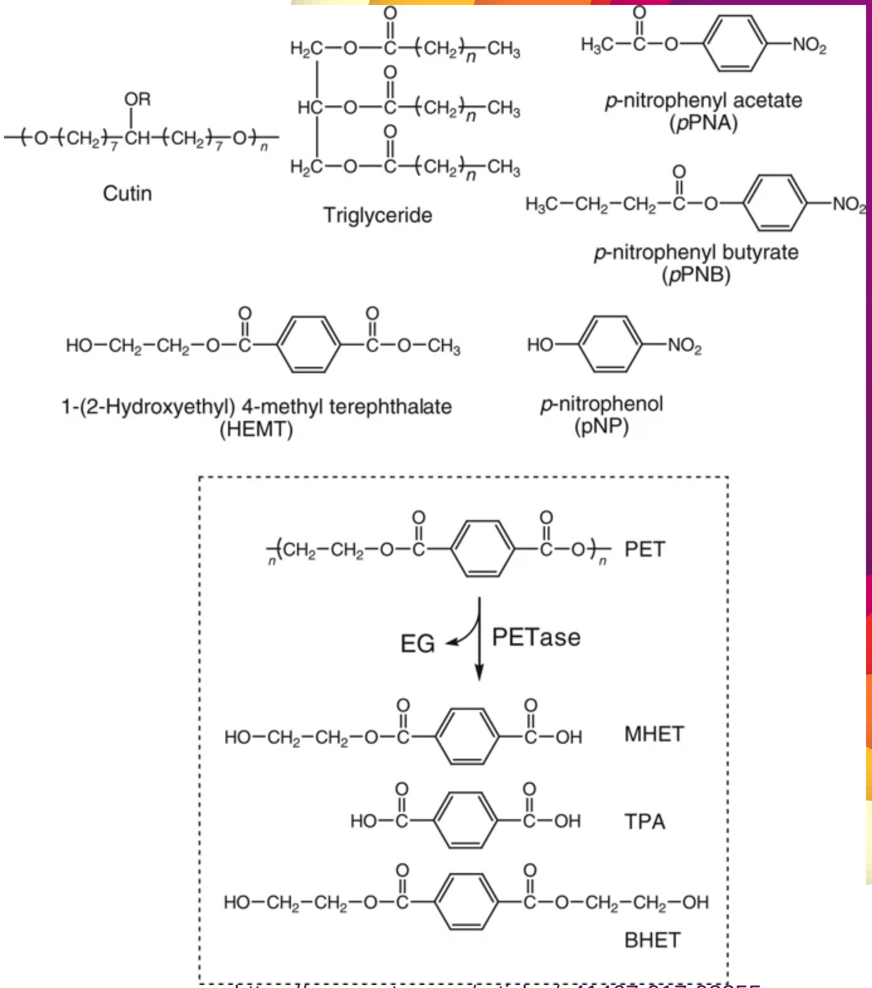
Goal of the Research

- Identify the structure and enzymatic kinetics of PET hydrolases
- To investigate the properties of PET materials and their hydrolysis

Methodology

Structure of PET Hydrolases

- Han et al. (2017)
  - Hydrolases that break down plastic include: Terephthalic acid (TPA), ethylene glycol (EG), mono-(2-hydroxyethyl) terephthalate (MHET), and bis(2-hydroxyethyl) terephthalate (BHET)

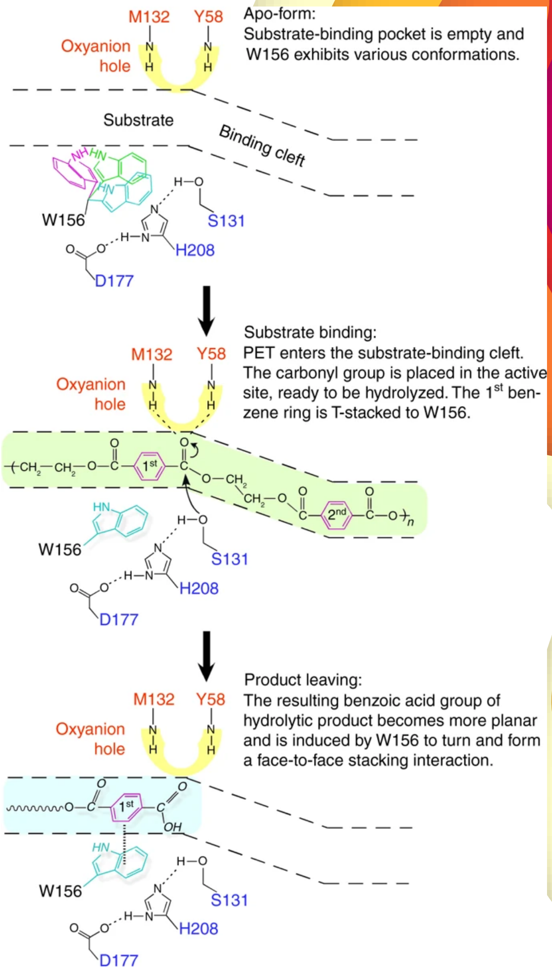


https://www.nature.com/articles/s41467-017-02255-z

Methodology

Enzymatic kinetics of PET hydrolases

- Han et al. (2017)
  - This figure shows the catalytic pathway of PETase
  - Once, the enzyme bonds to the PET, reaction occur that initiate a multitude of nucleophilic attacks on the PET causeing it to break down and begin to degrade



Methodology

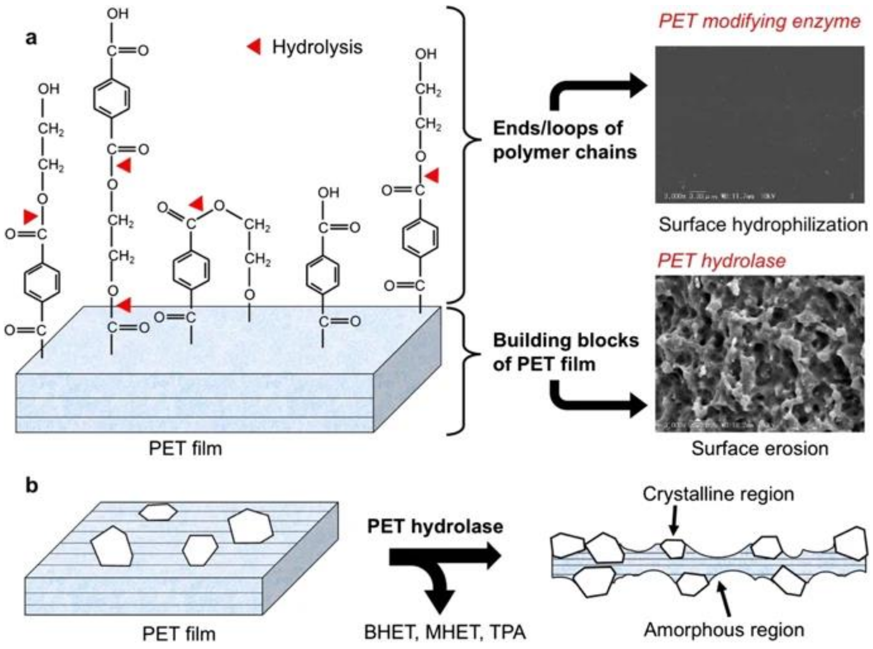
Properties of PET materials

- Han et al. (2017)
  - PET has a high molecular weight and is composed of ester bond-linked terephthalate (TPA) and ethylene glycol (EG)
  - PET has high durability but due to its properties is insoluble and unable to naturally degrade
- Barth et al. (2015)
  - The enzymatic degradation of PET requires milder temperature and pH conditions and thereby a lower energy consumption

Previous Results

- Muller et al.
  - PET was effectively depolymerized by a hydrolase from the actinomycete *Thermobifid a fusca*.
  - Erosion rates of 8 to 17 µm per week were obtained upon incubation at 55 °C.
- Vertommen et al.
  - The enzyme was stable
  - Hydrolysis rate on the amorphous PET maintained at sufficient high level over a long period of time of at least five days.

Previous Results



https://link.springer.com/article/10.1007%2Fs00253-019-09717-y

Discussion

Table 2. Weight loss of melt pressed PET films incubated with lipases from TfH, CaL, and PsL at 55 °C (and at 40 °C for PsL) in buffer at pH 7.

Sample	Weight loss %			
	1 week	2 weeks	3 weeks	Blank test
PET-B/TfH	10.3 ± 0.3	30.8 ± 0.1	22.4 ± 1.3	−0.1 ± 0.1
PET-B/TfH (1 test)	n.d.[a]	30.6 ± n.d.[b]	n.d.	n.d.
PET-G/TfH	14.1 ± 0.3	33.7 ± 0.3	49.7 ± 1.0	−0.1 ± 0.1
PET-B/rTfH	11.7 ± 1.6	27.3 ± 1.2	43.1 ± 1.6	−0.1 ± 0.1
PET-G/rTfH	14.6 ± 1.2	33.0 ± 1.0	54.2 ± n.d.	1.3 ± 0.2
PET-B/CaL	−0.3 ± 0.1	−0.1 ± 0.1	−0.6 ± 0.1	0.3 ± 0.1
PET-G/CaL	0.1 ± 0.1	0.4 ± 0.1	0.4 ± 0.0	−0.2 ± 0.1
PET-B/PsL (40 °C)	n.d.	n.d.	n.d.	0.4 ± n.d.
PET-B/PsL (55 °C)	0.2 ± 0.1	−0.1 ± 0.2	−0.2 ± 0.1	0.2 ± 0.1
PET-G/PsL (55 °C)	−0.3 ± 0.1	0.3 ± 0.1	0.1 ± 0.1	−0.5 ± 0.1

[a] n.d.: not determined.
[b] After 12 days.

Discussion

- Application:
- Enzymatic surface modification
  - more efficiently recycle PET
  - reduce the size of landfills.
- Significance
  - getting rid of plastic waste will clean out landfills
  - clean oceans of plastic pollution
  - protect more wildlife
- Limitations:
  - limited knowledge on enzymes which can successfully breakdown PET
  - Limited knowledge on the waste products of enzymatic degradation

Conclusion

- Commercial PET (Muller et al.)
  - can be effectively hydrolyzed by an enzyme at a rate that does not exclude a biological recycling of PET as previously thought.
- Recycling of polyester (Venkatachalam et al.)
  - has become an important process
  - has given commercial opportunity due to wide spread use and availability of PET bottles, packages and fibers.

Future Research

- Identify a PET hydrolases that can be applied for direct digestion of (Kawai et al.)
  - PET bottles
  - Textiles
  - Biaxially stretched films

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Works Cited

Aust, A. (2017, April 15). How Much Plastic Do You Use In a Day? Retrieved from https://ww2.kqed.org/education/2017/04/14/how-much-plastic-do-you-use-in-a-day/

Parker, L. (2019, June 7). The world's plastic pollution crisis explained. Retrieved from https://www.nationalgeographic.com/environment/habitats/plastic-pollution/

Kawai, F., Kawabata, T. & Oda, M. Current knowledge on enzymatic PET degradation and its possible application to waste stream management and other fields. *Appl Microbiol Biotechnol* **103,** 4253–4268 (2019). https://doi.org/10.1007/s00253-019-09717-y

Siracusa, V., Rocculi, P., Romani, S., & Rosa, M. D. (2008, July 18). Biodegradable polymers for food packaging: a review. Retrieved from https://www.sciencedirect.com/science/article/pii/S0924224408002185Webb, H., Arnott, J., Crawford, R., & Ivanova, E. (2012). Plastic Degradation and Its Environmental Implications with Special Reference to Poly(ethylene terephthalate). *Polymers*, *5*(1), 1–18. doi: 10.3390/polym5010001

Shen, L., & Worrell, E. (2014, May 9). Plastic Recycling. Retrieved from https://www.sciencedirect.com/science/article/pii/B9780123964595000131

Venkatachalam, S., Nayak, S. G., Labde, J. V., Gharal, R., Rao, K., & Kelkar, A. K. (2012, September 26). Degradation and Recyclability of Poly (Ethylene Terephthalate). Retrieved from https://www.intechopen.com/books/polyester/degradation-and-recyclability-of-poly-ethylene-terephthalate-

Vertommen, M. A. M. E., Nierstrasz, V. A., Veer, M. van der, & Warmoeskerken, M. M. C. G. (2005, August 22). Enzymatic surface modification of poly(ethylene terephthalate). Retrieved from https://www.sciencedirect.com/science/article/pii/S016816560500324X?casa_token=atO0v3fI39oAAAAA:WhyOeVx9q6ExqFMZ6VFFxvuL1UpIuOO494-07glVx5ymZ9SVaHxkZF_NDbsSQWXRsc1dJvXZ3B

How plastics are made. (n.d.). Retrieved from https://www.plasticseurope.org/en/about-plastics/what-are-plastics/how-plastics-are-made

Plastics-Chemistry Safety Facts. (n.d.). Retrieved from https://www.chemicalsafetyfacts.org/plastics/

Schrader, H., Profe, J., & Dresler, K. (2005, August 22). Enzymatic Degradation of Poly(ethylene terephthalate): Rapid Hydrolyse using a Hydrolase from T. fusca. Retrieved from https://onlinelibrary.wiley.com/doi/abs/10.1002/marc.200500410

Han, X., Liu, W., Huang, J.-W., Ma, J., Zheng, Y., Ko, T.-P., … Guo, R.-T. (2017, December 13). Structural insight into catalytic mechanism of PET hydrolase. Retrieved from https://www.nature.com/articles/s41467-017-02255-z

Barth, M. (2015, January). Effect of hydrolysis products on the enzymatic degradation of polyethylene terephthalate nanoparticles by a polyester Hydrolase from Thermobifida fusca. Retrieved from https://www.researchgate.net/publication/267341266_Effect_of_hydrolysis_products_on_the_enzymatic_degradation_of_polyethylene_terephthalate_nanoparticles_by_a_polyester_Hydrolase_from_Thermobifida_fusca

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