Solution Architect for Global
Bioeconomy & Cleantech Opportunities

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Material Value Chains

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Report: PET glycolysis

ARVI Theme plastic and rubber

Subtask 4.1.1

Content

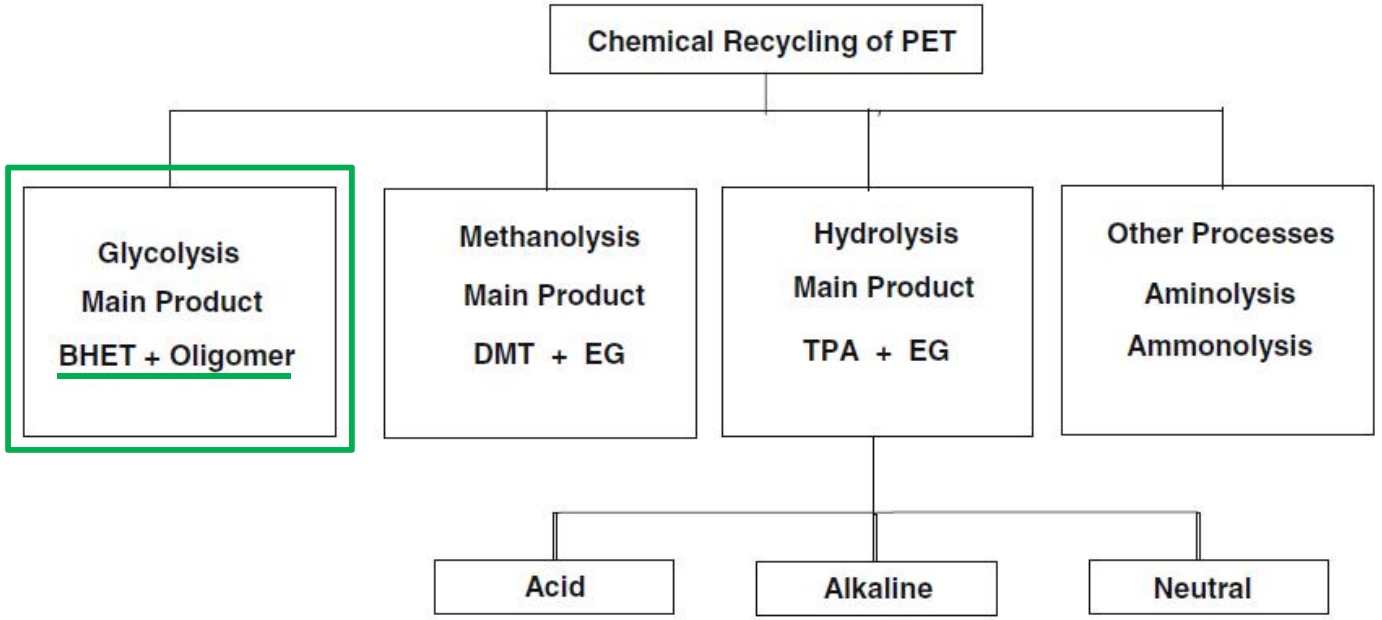
Brief Literature review

Experimental work and results

General Info on Poly(ethylene terephtalate)

- Poly(ethylene terephthalate) (PET) is formed by the reaction of terephthalic acid (TPA) and ethylene glycol (EG) or by the transesterification of dimethyl terephthalate and EG.
  - Starting materials are usually
    - BHET + EG or
    - DMT + EG
- Mechanical recycling may significantly decrease the PET properties.
- PET is a condensation polymer and thus it is possible to depolymerize it into its monomers and further depolymerize it to pristine polymer.

Chemical recycling routes for PET

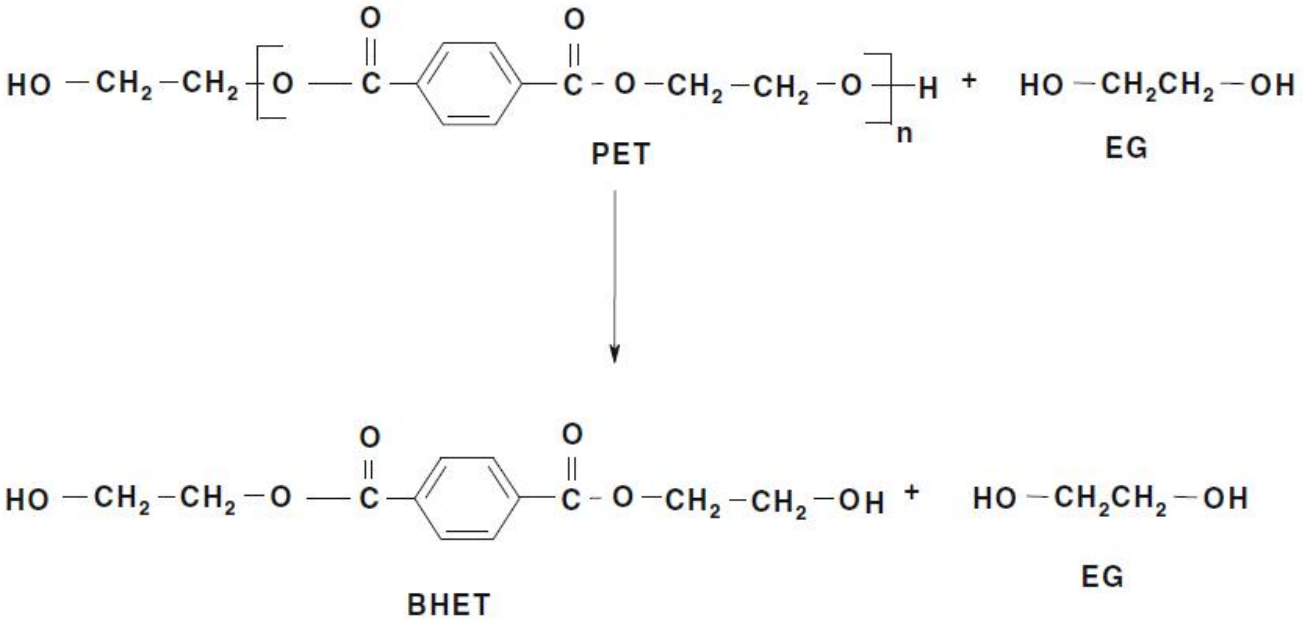


Sinha, Patel, Patel *J Polym Environ* (**2010**) 18:8–25

Glycolysis: Basic Information

- Glycolysis is chemical degradation of, e.g., polyester by glycol molecules in presence of trans-esterification catalysts, e.g., metal acetates. In the glycolytic reaction, ester linkages are broken and replaced with hydroxyl terminals.
- Most frequently used glycols are: ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), and dipropylene glycol (DPG).
- Reaction temperature range is 180 – 250 °C
- Reaction time range in 0.5 – 8 h
- Reaction pressure range 1 – 8 atm
- Catalyst: Zinc Acetate has been reported to be the most effective.

Glycolysis: PET Depolymerization by Ethylene Glycol



Sinha, Patel, Patel *J Polym Environ* (**2010**) 18:8–25

Glycolysis: Products

- The rection products of glycolysis are depending on the glycol used and reaction conditions.
- When EG is used and reaction is let to reach the end, the product is BHET.
- When PG is used the substitution of PG will take place and the products will have both 2-hydroxypropyl and 2-hydroxyethyl terminals. The product will be “BHE/PT”, i.e., a mixture of variants of bis(2-hydroxyethyl / 2-hydroxypropyl terephthalate).
- When the reaction has not reached the end or when equilibrium is formed, the products are polyester polyols with different lengths of ester oligomers including, for example 2 to 5 of primary polyester dimers (= dimer of terephthalic acid and ethylene glycol).

Experimantal: PET glycolysis setup

- Materials from Ekokem company:
  - Approx. 20 g of PET
  - 150 g of ethylene glycol (EG) or propylene glycol (PG)
  - Approx. 120 mg of zinc acetate dihydrate (0.5 w-% of $ZnAc_2$ for PET)
- Reaction vessel (Fig. 1):
  - 0.5 liter glass reactor with four neck cover equipped with an Allihn condenser and PTFE mixer; heated with an electromantle.
- Reaction conditions:
  - Temperature was approx. 190 °C (the electromantle was controlled with a thermostat set to 250 °C)
  - Reaction time was 3 – 5 hours at normal pressure.

Fig. 1

Summary of reactions

Reaction code	PET	Glycol and catalyst	Reaction temperature and time	Reaction products
EG1	Cleaned mixed color PET, 20 g	EG, 150 g ZnAc, 120 mg	190 °C, 5 h (EG was not boiling)	Solution and solid residual. According to FTIR and DSC, the solid residual is BHET.
PG1	Cleaned mixed color PET, 20 g	PG, 150 g ZnAc, 120 mg	188 °C, 5 h (PG was boiling)	Solution without residual. After distillation, a liquid/waxy residual with high viscosity was obtained. According to FTIR and DSC the residual was a mixture of polyester polyols with 1 – 4 repeating polyester dimers.
PG2	Cleaned colorless rPET, 20 g	PG, 150 g ZnAc, 120 mg	188 °C, 3 h (PG was boiling)	Solution without residual. After distillation, a liquid/waxy residual with high viscosity was obtained with same properties as that from PG1. After water precipitation, a solid product with same properties as the distillation residuals from PG1 and PG2.
PG3	Non-cleaned mixed color PET from “SUM”, 23 g	PG, 150 g ZnAc, 123 mg	188 °C, 5 h (PG was boiling)	Solution without residual. After water precipitation, a solid product with same properties as the distillation residual from PG2.

Summary

- Glycolysis of PET with EG resulted in a solid residual and reaction solution.
  - The FTIR and DSC analysis of the residual are supporting that the solid residual is BHET.
- Glycolysis of PET with PG resulted in almost no solid product. In the reaction solution there was a product component which was insoluble in water → precipitation took place when excess of water was added into the reaction solution.
- In addition to precipitation by water, reaction solutions were distilled in vacuum with rotary evaporator. The product was a sticky polyester wax with high viscosity and distinct odor.
- The FTIR analysis suggest that the water insoluble component and the distillation residual are similar compounds: polyester waxes with hydroxyl terminals, polyester polyols.
  - The gravimetric measurements suggest that the wax has approx. two repeating unit (dimer) of PET as its average molecule size.
- The DSC measurements reveal similar irreversible melting features for both distillation residual and water precipitates.
- It seems that the reaction product can be separated from the solution either by water precipitation or by distillation.
- The impurities had very small effect on the glycolysis reactions made in this project (PG1, PG2, and PG3).

Conclusions

- The reaction between cleaned PET and EG resulted in solid partly crystalline residual which consists most likely of BHET
- The reactions of different PET fractions with PG produced monomeric 2-hydroxypropyl terephthalate derivative and additionally longer polyester polyols with approximately 2 to 3 repeating polyester dimers and 2-hydroxypropyl terminals.
- In the reactions, the quality of PET starting material had only very small effect on the reaction and its products.

Future sights

- Next steps to proceed from PET glycolysis
  - Optimization of reaction conditions
    - Temperature, pressure, time
  - More define reaction products
    - Purity and separation
  - Scalability
    - Possibilities for scale-up, cost calculation / feasibility study
- Comprehensive study on the possible uses of reaction products as recycled raw materials for the manufacture of:
  - unsaturated polyester
  - polyurethane
  - epoxy resin
  - alkyd resin
  - vinyl ester resin

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