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Levente Kárpáti^{1*}, Györgyi Szarka², Mátyás Hartman³,
Viktória Vargha¹

RESEARCH ARTICLE

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Abstract

A new chemical way has been introduced to recycle poly(ethylene terephthalate) via acido-alcoholysis. Acido-alcoholysis has been developed as a green way to produce oligoesters from PET waste which can be used as building blocks to new compostable polyesters. Organic acids and 1,4-butanediol were used as reagents. The solvolysis products were further reacted with diglycidyl ethers of different diols to obtain higher molecular weight polyesters. The resulted materials were tested with GPC, FTIR, TGA, functional group analysis methods and composting. It was found that the reagents in acido-alcoholysis fully incorporated into the reaction product obtaining oligoesters with carboxyl and hydroxyl end groups. Significant mass loss and fragmentation was observed on oligo- and polyesters after composting.

Keywords

chemical recycling, PET, oligoesters, biodegradation

1 Introduction

Polyesters, especially poly(ethylene terephthalate) (PET) are widely used in industrial and research fields as advanced materials and in everyday life for packaging, fibers and various plastic products. Due to its wide range of application huge amounts accumulate in industrial and domestic waste. There are several methods to recycle PET waste namely, primary, secondary, tertiary and quaternary recycling. [1-3] The primary method consists in recycling primary preconsumer industrial polymer scrap back into the production process. The secondary method is the well known collection, separation and reprocessing of consumer polymer waste. The tertiary method is chemical recycling to obtain various chemicals and to produce new materials. The quaternary recycling method is incineration and pyrolysis.

In our research we study the chemical recycling of PET waste in order to produce value added products. There are several well known solvolytic methods such as alcoholysis (glycolysis and methanolysis), aminolysis, ammonolysis and hydrolysis. [4-18] The main purpose of these methods is to obtain different chemicals, mostly monomers for the reproduction of polyesters. The methanolysis, glycolysis and hydrolysis of PET results in terephthalic acid or its esters and ethylene glycol that can be used to reproduce PET with properties equal to the virgin material. [19-21] Terephthalic amides, diamides obtainable via amino and ammonolysis, can be used as cross-linkers for thermosetting resin production.

Alcoholysis is a well known method in organic chemistry, fundamentally it is a transesterification reaction using alcohols (Scheme 1). In industrial and research areas methanol, ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, and other oligomer diols are widely used for PET depolymerisation. The usual conditions for these reactions are assumingly 180-220°C, at atmospheric pressure in inert gas atmosphere in the presence of a catalyst. [4-9] The reaction conditions may vary, higher temperatures and pressurized reactors, even supercritical conditions have been used in previous studies. [22-23]

Methanolysis and glycolysis serve as a way to recover and reuse ethylene glycol, terephthalic acid or dimethyl terephthalate or bis(hydroxyethyl)terephthalate (BHET) for PET

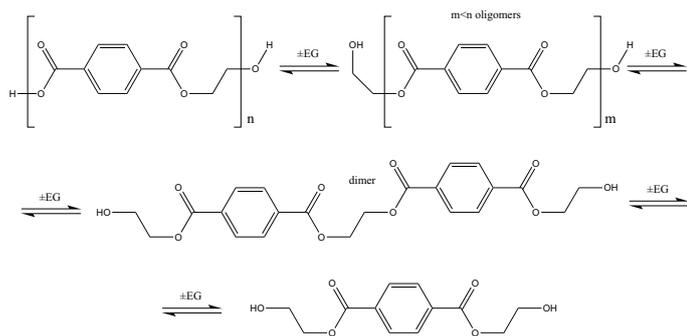
¹Laboratory of Plastics and Rubber Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, 1111 Budapest, Műegyetem rkp. 3., Hungary

²Polymer Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Center for Natural Sciences, Hungarian Academy of Sciences, 1117 Budapest, Magyar tudósok körútja 2., Hungary

³Zöld Híd Régió Nonprofit Kft., H-2100 Gödöllő, Dózsa Gy. út 69., Hungary

*Corresponding author, e-mail: karpati.levente@mail.bme.hu

production. Doing so considerable number of research papers focus on optimizing the yield of BHET productions. The equilibrium nature of the transesterification reaction causes the appearance of several higher molecular weight side products (dimers and oligomers). Thus a wide range of catalysts were studied and introduced, including metal salts, ionic liquids, heterogeneous catalyst like magnetic nanoparticles and MOFs (metal-organic frameworks) to enhance BHET yield. [24-40] High ratio of ester:alcohol (1:3-1:8) were used in these studies to shift the equilibrium to the BHET production. The reaction product was recrystallized from water or other good solvents of BHET. The insoluble side products (oligomers) weren't used further.



Scheme 1 Glycolysis of PET

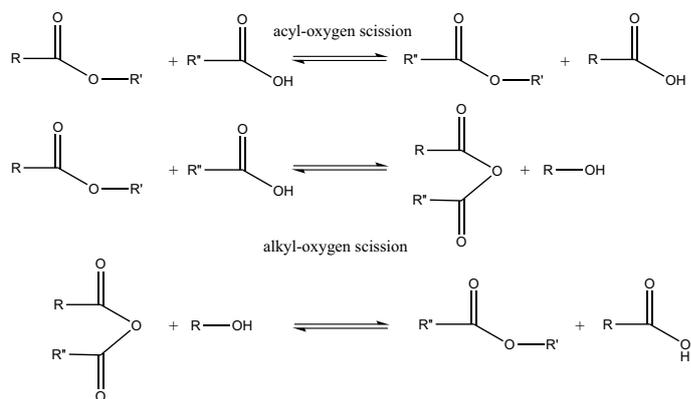
Other studies focused on resin and other PET based polymer production by using lower PET:alcohol ratios (1:1-1:3) for glycolysis. [7-9] In some cases, the glycolysis products were further used without any purification steps [41-43]. Our own experience (unpublished results) and other studies on glycolysis show molecular mass distribution usually with well distinguishable peaks. [6, 8, 44]

We would like to propose a method to incorporate lower molecular weight side products of glycolysis (diols and oligomers as well) in order to obtain oligomers with somewhat uniform molecular mass that can serve as building blocks for new polyester materials. Hence no purifications steps are needed for further use. We introduced a rarely used method for PET solvolysis and combined it with glycolysis. In classical organic chemistry it is known that organic acids can be used for transesterification reactions as well. This method was used to produce several low molecular weight organic monoesters from diesters and vinyl esters. [45-49] Acidolysis reaction is a classical reaction of esters where an acid is used to break the ester linkage to produce a new ester. It has two possible routes, alkyl-oxygen and acyl-oxygen scission. Via acyl-oxygen scission an anhydrite intermediate is produced that can react with an alcohol (Scheme 2). [45]

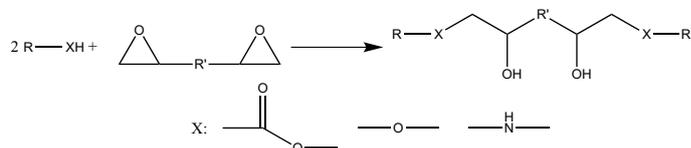
In this study the amount of acid and alcohol are comparable to each other, both acidolysis, alcoholysis and esterification of acids can occur in the same system. We propose acido-alcoholysis as a way to produce PET based hydroxyl and carboxyl

terminated oligomers without low molecular weight side products. These oligoesters can be further used without any purification steps, hence shortening the recycling process.

Organic acids (adipic, succinic and sebacic acid) and 1,4-butanediol as solvolytic agents were applied in PET acidolysis and acido-alcoholysis reactions. We used diglycidyl ethers to obtain high molecular weight polyesters. Diglycidyl ethers can be used as chain extenders. [49-50] These compounds can react with hydroxyl-, carboxyl- and amine groups as well (Scheme 3), although their reactivity differs for each functional group. [51-53] The presence of carboxyl group in our system was expected to result in higher molecular weight products and fast reactions. Our goal was to develop a method capable to produce semi-aromatic, compostable polyesters derived from PET waste.



Scheme 2 Acyl-oxygen and alkyl-oxygen scission during acidolysis



Scheme 3 Chain lengthening with diglycidyl ethers of diols

2 Experimental

2.1 Materials

PET flakes from HUKÉ Kft. (Sárvár) were used for solvolytic reactions. The consumer (bottle) PET waste was washed and ground to small flakes (thickness 0.41 ± 0.08 mm; (9.9 ± 2.9) mm) \times (6.8 ± 2.2) mm). Adipic acid, sebacic acid, succinic acid and 1,4-butanediol were purchased from Sigma Aldrich. 1,4-butanediol diglycidyl ether (RD3), 1,4-cyclohexanedimethanol diglycidyl ether (RD11) and 1,6-hexanediol diglycidyl ether (RD18) are products of IpoX Chemicals. Zinc-acetate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) was purchased from BDH Chemicals and was used as catalyst. Tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) were purchased from Molar Chemicals and were used as solvents. Dibutyltin-dialurate, perchloric-acid, methyl-cellosolve and di-n-butylamine were purchased from Molar Chemicals and were used for hydroxyl group measurements. All the reagents were used without further purification.

2.2 PET solvolysis procedure

All the solvolytic reactions were carried out in a 250 cm³ four-necked round bottom glass flask equipped with mechanical stirrer, inert gas inlet, thermometer and reflux condenser. All the reactions were carried out at 210 °C in argon atmosphere at atmospheric pressure. All the components were weighed into the reactor at the beginning of the reactions. The ratio of the reagents was calculated to the repeating unit of PET (192.18 g*mol⁻¹). Acidolysis reactions were conducted with 1:1 PET:acid molar ratio with adipic acid, succinic acid and sebacic acid. Alcoholysis reaction was carried out with 1:1 PET/alcohol molar ratio with 1,4 butanediol. Acido-alcoholysis reactions were carried out with 1:0.5:0.5 PET:acid:alcohol molar ratio with each one of the acids and 1,4 butanediol. The complete disappearance of the PET flakes was considered as the end of the reactions. The reaction time varied with each reaction, in average it was 1.5-2.5 hours.

2.3 Chain extension

Chain extension of the acido-alcoholysis products was carried out in a 250 cm³ four-necked round bottom glass flask equipped with mechanical stirrer, gas inlet, thermometer and reflux condenser. The reactions were carried out at 180 °C in argon atmosphere. All the components were weighed into the reactor at the beginning of the reactions. The ratio of the reagents were stoichiometric, calculated to the total functional group content (total hydroxide + total carboxyl content). 1,4 butanediol diglycidyl ether (RD3) for all the solvolysis products. 1,4-hexanediol diglycidyl ether (RD18) and 1,4 cyclohexanedimethanol diglycidyl ether (RD11) were only used with sebacic acid/1,4-butanediol reaction product.

2.4 Methods of characterisation

The FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrometer. The wave number range was between 4000–400 cm⁻¹, the resolution 2 cm⁻¹, the number of scans was 28 with ATR, 16 with KBr pastilles. Solubility was checked in tetrahydrofuran (THF) and in N,N-dimethylformamide (DMF) before GPC measurements and functional group analysis. For the acid value 0.5000 g samples were dissolved in 20 cm³ THF or DMF. The samples were titrated with 0.5 M sodium hydroxide solution in methanol using phenolphthalein indicator. Hydroxyl value was determined via a titration method. 1.5000 g of sample were dissolved in THF or DMF. Than 10 cm³ of phenyl-isocyanate solution and 0.2 cm³ dibutyltin-dialurate catalyst solution was added to the solutions. After 15 minutes methyl-cellosolve and di-n-buthylamine was added. The samples were titrated with 0.5 M perchloric-acid solution in the presence of methyl red indicator. Gel permeation chromatographic (GPC) measurements were done using a Jetstream 2 plus thermostat, Waters HPCL Pump 515 and Waters Styragel HR1, 2, 4 column with tetrahydrofuran. Polystyrene standards were used for the calibration. Perkin Elmer TGA 7 was used

for thermogravimetric measurements. About 10 mg of samples were weighed in and measured in purging nitrogen gas with 10 °C/min heating rate up to 700 °C. Sheets of 100x100x0.6 mm were pressed in a laboratory press at 150 °C and 150 kN for composting tests. Pressed sheets were laid in compost for 6 weeks carried out by Zöldhíd Régió Kft (Hungary) via Gore™ Cover system. Green waste materials were chopped up and laid down into piles and covered with a semipermeable cover. The pressed sheets were put in nets inside the compost piles. The temperature was monitored and controlled by the automatic ventilation system and was kept at around 75°C. Weight loss and fragmentation was observed after the composting period.

3 Results and discussion

3.1 Characterization of solvolysis products

The FTIR spectra of the solvolysis products with sebacic acid and/or 1,4-butanediol are represented in Fig. 1. The measurements support that the reactions took place. Around 3600 cm⁻¹ wide low intensity peak appeared on the spectrum of PET waste indicating the negligible presence of hydroxyl groups. CH₂ valence vibration peaks at 2940 and 2850 cm⁻¹ have shown increase in intensity compared to PET. The ester carbonyl valence vibrations at 1721-1700 cm⁻¹ shifted from 1712 to 1720 cm⁻¹ indicating the appearance of aliphatic ester groups. The spectrum of acidolysis products showed double peak or at least shouldered peak for carbonyl valence vibrations. This is an indication of the appearance of at least two kind of carbonyl compounds in the products. Changes between 1500-1300 cm⁻¹ and 1100-900 cm⁻¹ are observable in the IR spectrum indicating changes in molecular structure. The differences and changes in carbonyl and hydroxyl groups after the reactions was further studied with functional group analysis.

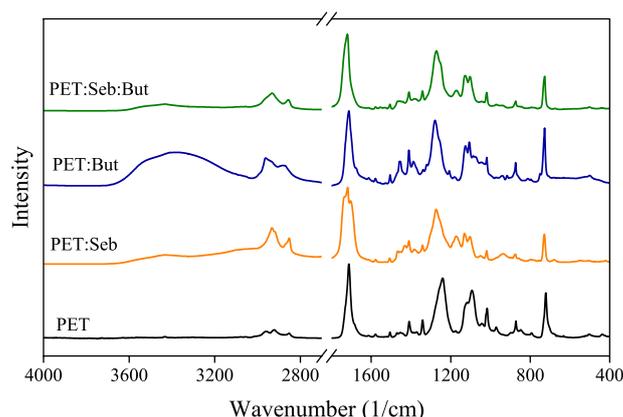


Fig. 1 PET and its solvolysis products, FTIR spectrum

Acid values were measured with a standard titration procedure with NaOH solution in THF, the OH values were measured with phenyl-isocyanate method (Table 1). The theoretical values were calculated according to the added quantity of acid and/or hydroxyl groups. Acid values in acidolysis

are close to the calculated ones, while they decreased during acido-alcoholysis. The slight increase in acid value can be attributed to the formation of terephthalic acid. The decrease during acido-alcoholysis can be explained by the occurrence of esterification reaction between the diacids, diols, dimers and oligomers. The major decrease in case of PET:SucAc can be attributed to the longer reaction time. Compared to the other acidolysis reactions it took twice the time (~ 4 hours) for the PET to completely disappear, thus esterification reaction had more time to occur.

Table 1 Acid and hydroxyl values of PET solvolysis products

Sample	Theoretical		Product	
	Acid value (mmol*g ⁻¹)	OH value (mmol*g ⁻¹)	Acid value (mmol*g ⁻¹)	OH value (mmol*g ⁻¹)
PET:Adac	5.91	-	6.36	-
PET:Sucac	6.46	-	5.14	-
PET:Sebac	5.07	-	4.83	-
PET:But	-	7.13	-	6.41
PET:Adac:But	3.20	3.36	0.96	0.19
PET:Sucac:But	3.36	2.93	0.77	0.51
PET:Sebac:But	2.93	2.43	1.13	0.16

White, powdery residuum was observed after dissolving our acidolysis products in THF. The powder was filtered; washed and dried. FTIR spectra was recorded and compared to terephthalic acid (99 %, Molar Chemicals) in KBr pastilles. The spectra were found to be identical, thus proving the formation of terephthalic acid.

GPC measurement results of PET acidolysis and alcoholysis products are represented in Fig. 2-3 and given in Table 2. THF was used as a solvent for the GPC measurements, thus PET waste couldn't be compared directly to the reaction products,

due to its insolubility. Thus the solubility of the reaction products proves the success in depolymerisation. Calibration and the comparison to solvolytic reagents were used to determine the success of the solvolysis. The molecular mass distributions of the pure acidolysis and alcoholysis products showed similarities. The gel permeation chromatograms showed several peaks including the used solvolytic reagent (adipic-, succinic-, sebacic acid and 1,4-butanediol). In case of acidolysis with sebacic acid (Fig. 2 a)) a new peak appeared at higher retention volume, indicating a slightly lower molar weight side product than sebacic acid. According to the mechanism of acidolysis (Scheme 2) the possible eliminates of the reaction are terephthalic acid and ethylene glycol. We put the chromatogram of ethylene glycol as a reference. Hence we propose, the new peak is attributed to the newly formed terephthalic acid. This result is explained by the fact that the molecular weights of succinic and adipic acid are close enough to terephthalic acid to make their peaks indistinguishable on the chromatograms. The significantly higher molecular weight of sebacic acid allowed the separation of the two acids, thus two separate peaks appeared. Adipic acid was the only acid that remained in significant amount after the acidolysis. The proven elimination of terephthalic acid and high amount of adipic acid residuum could have caused acid value higher than theoretical.

Fig. 2 b) shows a GPC chromatogram of classical glycolysis products with distinct peaks previously stated in the introduction. The peaks can be connected to oligo- and diesters of terephthalic acid with butane-diol and ethylene glycol. A minor butane-diol residuum can be observed as well.

No reagent moieties could be traced in the acido-alcoholysis products (Fig. 3). Compared to acidolysis and alcoholysis the peak shifted to lower retention volumes. Consequently, acido-alcoholysis is more efficient than either acidolysis or alcoholysis in oligoester production, all the used reagents were incorporated

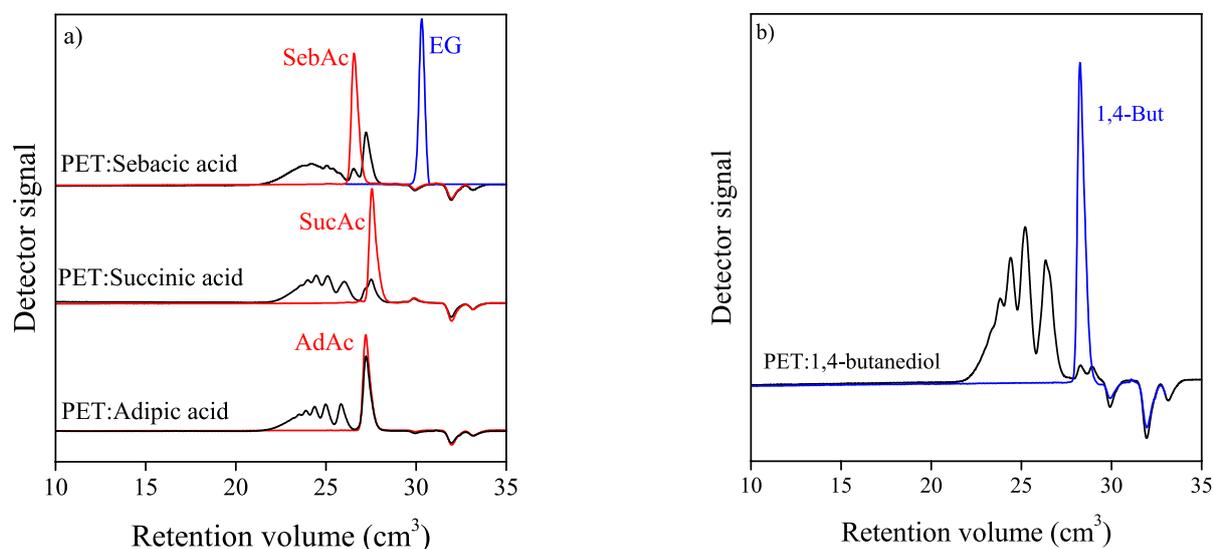


Fig. 2 GPC chromatogram of PET solvolysis product with sebacic-, succinic-, adipic acid and 1,4-butanediol

into the products. The higher average molar weight and decrease in acid and hydroxyl value proves, and supports this statement (Table 2). The functional group analysis and the GPC measurements correlate. As expected higher molecular weight products showed lower functional group content.

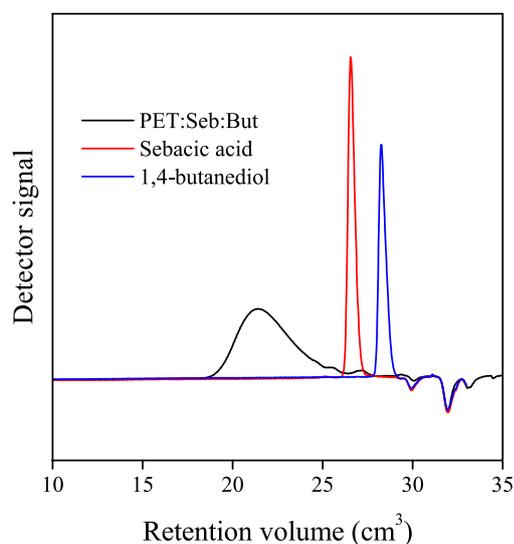


Fig. 3 PET solvolysis product GPC chromatogram with sebacic acid and 1,4 butanediol

Table 2 Molecular weight averages of the solvolysis products of PET waste

Sample	M_n (g* mol^{-1})	M_w (g* mol^{-1})	M_w/M_n
PET:Adac	590	920	1.6
PET:Sucac	650	970	1.5
PET:Sebac	640	1000	1.6
PET:But	710	980	1.4
PET:Adac:But	2100	4200	2.0
PET:Sucac:But	1800	3400	1.9
PET:Sebac:But	2400	4700	2.0

Thermogravimetric analysis (TGA) further supports our statement of oligomer production (Fig. 4). The derivative curves (DTG) were calculated in order to determine the changes in slope in weight loss and starting temperatures of each step. Any early weight loss (1-2%), below 100 °C can be connected to impurities within the PET waste. Solvolysis with 1,4-butanediol resulted in distinct dimers and oligomers causing a constant, multi-stepped weight loss via evaporation starting at 103 °C until it reached its thermal degradation temperature at 312 °C than 392 °C. The acidolysis product with sebacic acid shows a two-step degradation curve with a major change in the slope of the curve around 400 °C. In this case the first degradation step started at 265 °C, then the change of slope occurred at 409 °C. Acido-alcoholysis products showed only one major degradation step starting at 390 °C indicating a more uniform composition than the previously discussed reaction products.

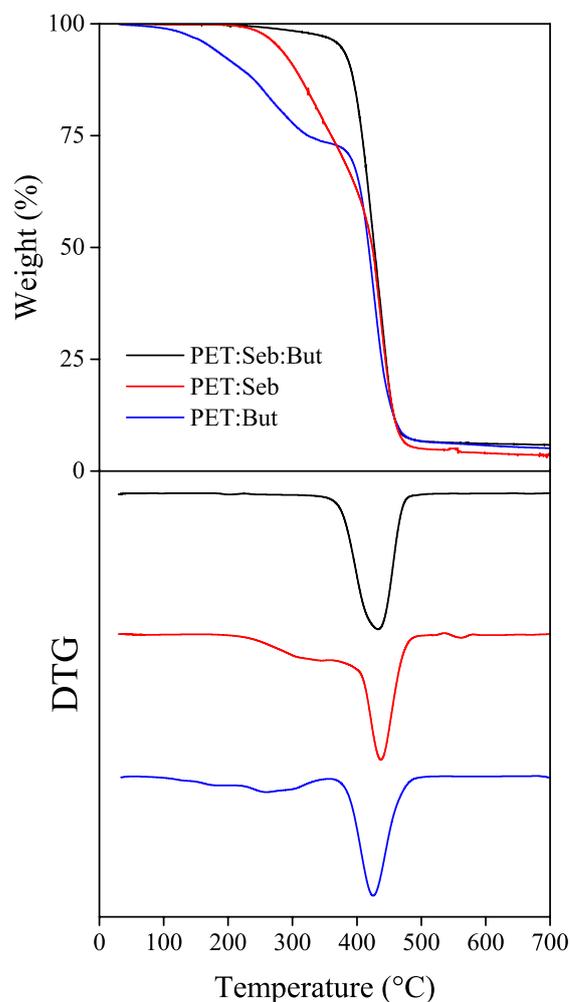


Fig. 4 TGA measurements and DTG curves of solvolysis products

3.2 Chain extension of PET solvolysis products

Each of the chain extenders show multiple peaks on the GPC chromatograms. These extenders are commercial reactive diluents recommended for epoxy resins. The exact composition and components are unknown, except their main components given previously. They were weighed in and used according to the functionality given in the technical data sheets available from the manufacturer.

The GPC chromatograms of the chain-extended samples and the reagents are represented in Fig. 5. The molecular mass value averages and polydispersity are given in Table 3. The GPC results unequivocally proved the molecular weight increase after chain extension. Our GPC column system's effective molecular range according to the manufacturer is about 600000 but a calibration curve with polystyrene standards up to 2 520 000 could be done.

The chain lengthening was successful and polymers with broad molecular weight distribution were produced containing polymer chains higher than 100 000. We have to note that the samples only partially dissolved for the GPC measurements, thus the data only represent the dissolved components of the products. The extreme difference in number and weight average molecular weights can be connected to this problem. RD3 and RD11 caused

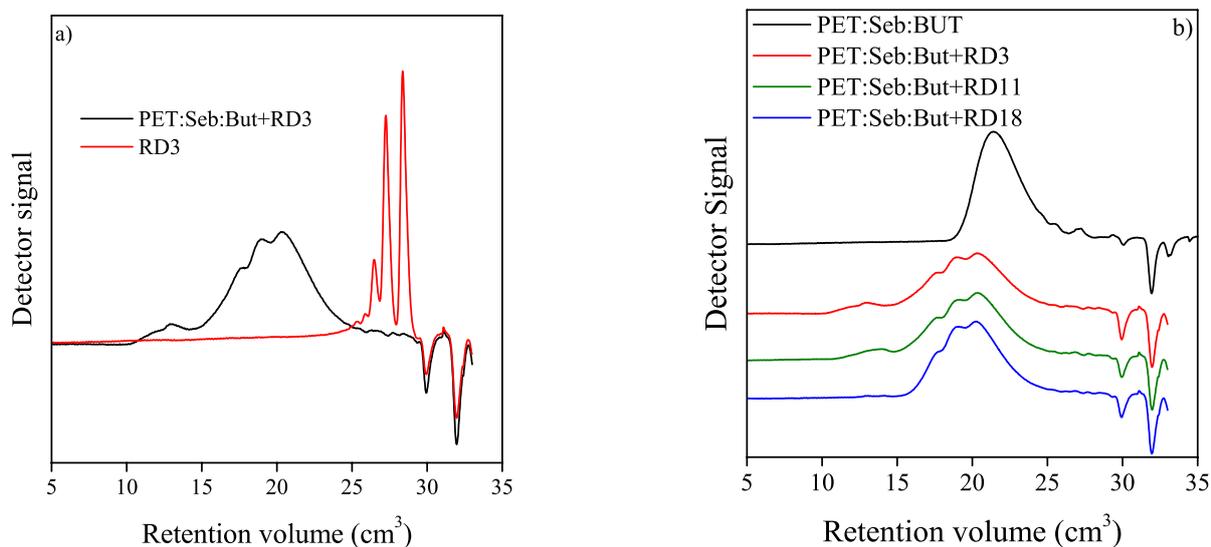


Fig. 5 GPC chromatograms of the chain extended products

Table 3 Molecular weight averages of the chain extended products

Sample	M_n (g* mol^{-1})	M_w (g* mol^{-1})	M_w/M_n
PET:Adac:But+RD3	3800	318 000	83.7
PET:Sucac:But+RD3	3500	148 000	42.3
PE:Sebac:But+RD3	6200	380 000	61.3
PET: Sebac:But+RD11	5600	232 000	41.4
PET:s Sebac:But+RD18	5600	30 000	5.4

extremely wide distribution in all cases. These reactive diluents might have components with higher epoxy functionality than 2 that could have caused branching during chain lengthening.

The FTIR spectrum of a chain-extended product are shown in Fig. 6. The FTIR diagrams prove that the diglycidyl ethers reacted with the solvolysis products. The solvolysis products showed no traces of epoxy group. The characteristic valence vibrations of epoxy groups (912 and 840 cm^{-1}) were absent in the chain extended products. Due to the presence of carboxyl groups the reaction with the glycidyl ethers was rather intense. The carboxyl groups have catalytic effect in the reaction of epoxy with hydroxyl groups [51-53].

3.3 Composting

The used composting method provides an insight into the practical degradability of these materials. Naturally propagated microorganisms turned the green waste to compost and degraded the pressed sheets. The pressed sheets were kept in nets to prevent the fragments to fall in and mix with the compost. The produced materials had reasonable rate of degradation and fragmentation after 6 weeks (Table 4). All the studied press compressed plates disintegrated into small pieces (Fig. 7). The chain extended products showed somewhat lower degradation rate, due to their higher average molecular mass. These degradation rates may be increased with longer composting time.

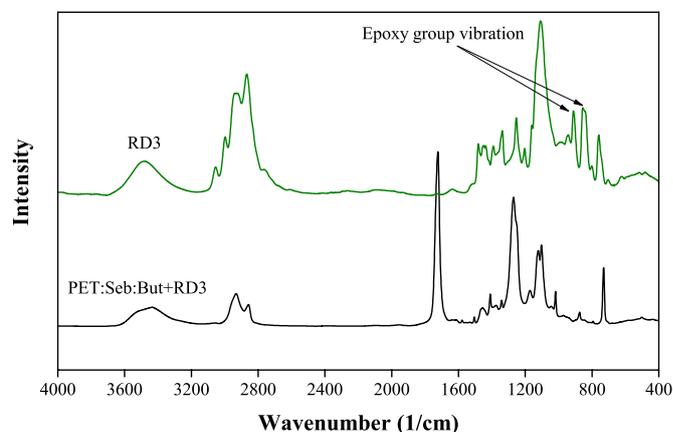


Fig. 6 FTIR spectrum of the chain extended product

Table 4 Weight loss of solvolysis- and chain-extended products after compostation

Sample	Weight loss in compost (m/m %)
PET:Adac:But	50.8
PET:Sucac:But	62.0
PET:Sebac:But	51.5
PET:Adac:But+RD3	35.6
PET:Sucac:But+RD3	36.9
PET:Sebac:But+RD3	24.7

4 Conclusions

A new method, acido-alcoholysis was successfully developed for the chemical recycling of PET. Acido-alcoholysis was investigated and proved to be efficient in incorporating the solvolytic agents and producing higher molecular weight oligoesters. The GPC data suggest that both acidolysis and alcoholysis products contain the used reactants, and consist of distinct oligoesters while in the products of acido-alcoholysis no trace of the reagents could be detected by GPC



Fig. 7 Composting residuum of PET:Sebacic acid:1,4-butanediol (paperclip for scale)

analysis. The functional group analysis, GPC chromatograms and FTIR spectra proved the success of the depolymerization. Thermogravimetry has also supported our theory on acido alcoholysis resulting in products of more uniform structure. Semi-aromatic polyesters were prepared via chain-lengthening with glycidyl ethers. Substantial increase in molecular weight was achieved. Reasonable weight loss and fragmentation was observed after 6 week-long composting of poly- and oligoesters.

Acido-alcoholysis is a new promising way to chemically recycle PET waste and to produce higher molecular weight oligoesters. These oligoesters can be used as building blocks for new compostable semi-aromatic polyesters. In the future we would like to further investigate and explore the opportunities of this method and combine it with polycondensation.

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