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Application of waste poly(ethylene terephthalate) in the synthesis of new oligomeric plasticizers

Ewa Langer [a], *, Sylwia Waśkiewicz [b], Marta Lenartowicz-Klik [a], Krzysztof Bortel [a]

[a] Institute for Engineering of Polymer Materials and Dyes, 87-100 Toruń, ul. M. Skłodowskiej-Curie 55, Poland
[b] Silesian University of Technology, Faculty of Chemistry, 44-100 Gliwice, ul. Strzody 9, Poland

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ABSTRACT

New method of transesterification of waste poly(ethylene terephthalate) (PET) with aliphatic oligoesters was developed. The structures of obtained oligoesters were identified by NMR, ESI-MS and SEC methods, and then correlated with physical properties determined by DSC and TGA analyses. Physico-chemical properties of synthesized plasticizers were compared with monomeric and polymeric commercial products. Products of the reaction of PET with oligoesters based on azelaic acid with 1.4-butanediol and adipic acid with triethylene glycol occurred to be remarkable substitutes of commercial plasticizers. They possessed lower volatility and much higher thermal stability. Insertion of glycerol unit into aliphatic oligoester and using it for the process of PET depolymerization resulted in obtaining of plasticizers of branching structure with glycerol unit as a core. They possessed lower viscosity and higher molecular mass in comparison with their linear equivalents.

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most commonly used engineering plastics which owes its popularity to its mechanical properties, chemical resistance, clarity, low O_2 and H_2O permeability, and good rigidity/weight ratio. The use of poly(ethylene terephthalate) has increased significantly in recent years since its introduction as a material for the production of beverage packaging. Moreover, it is widely used in the textile industry, high strength fibres and photographic films. PET itself is not directly hazardous for the natural environment but it does make up a considerable volume of all the municipal waste ending up in landfills. It does not erode due to its high resistance to weathering and biological agents. PET is a non-degradable plastic in normal conditions, as there is no known organism that can consume its relatively large molecules [1]. However PET is one of the most extensively recycled polymeric materials.

There are three distinct approaches to the recycling of post-consumer plastic packaging materials. The Environmental Protection Agency (EPA) has adopted a new extensive nomenclature that refers to physical reprocessing as secondary recycling (2°) and chemical processing as tertiary recycling (3°). The EPA primary recycling (1°) refers to the use of pre-consumer industrial scrap and salvage to form new packaging, a common product in industry [2].

There are numerous chemical ways of recycling PET, which include: hydrolysis, alcoholysis, aminolysis, acidolysis, glycolysis and transesterification. PET is chemically re-processed by its total depolymerization into monomers or partial depolymerization into oligomers and other products [3]. Table 1 presents the chemical methods of chemical recycling of PET, the main reactants and the products obtained [4–8].

The utilization of PET waste generates value-added products such as unsaturated polyester resins, oligo- or polyester plasticizers, acrylate/methacrylate terminated oligoesters and raw materials for polyurethanes [5–8]. Our study focused on oligoester plasticizers obtained by means of the chemical recycling of PET.

The most commonly used plasticizers are monomeric plasticizers, such as: phthalates, adipates and benzoates. Their disadvantages include lower resistance of the bond line to heat and possible migration. However, the use of phthalic plasticizers has been on the decrease due to their toxicity and tendency to sweat out. Some companies and sectors have looked for safer materials as alternatives to certain phthalates. While oligomeric plasticizers have smaller plasticizing ability compared to monomeric plasticizers, they exhibit limited volatility and migration and do not undergo extraction, which is essential in many applications [9].

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* Corresponding author.
E-mail address: e.langer@impib.pl (E. Langer).

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Table 1
Methods of chemical recycling of PET.

Method	Reactant	Reaction products
Hydrolysis	Water	Terephthalic acid and ethylene glycol
Alcoholysis	Methanol	Dimethyl terephthalate and ethylene glycol (1.2-ethane diol)
Aminolysis	Amine	Terephthalamide
Glycolysis	Ethylene glycol	Bishydroxyethyl terephthalate and ethylene glycol

There are many publications in the literature on obtaining dioctyl terephthalate (DOTP) in the process of PET alcoholysis. There are few studies, however, that describe the synthesis of oligomeric plasticizers based on the products of PET waste depolymerization. For instance, Dupont et al. [10] reported on the alcoholysis of PET scrap using 2-ethyl-1-hexanol (EH) at reflux temperature for the purpose of synthesizing DOTP plasticizers for flexible poly(vinyl chloride) (PVC). The DOTP produced by this method was equivalent to commercial grades in terms of its plasticization efficiency for PVC.

Dutt and Soni, on the other hand, synthesized an oligomeric plasticizer with an average molecular mass in the range of 450–900 g/mol from PET waste also through alcoholysis using EH. They used it in nitrile rubber and nitryle-PVC blends [11].

The boiling point of EH at atmospheric pressure is about 180 °C and the efficiency of alcoholysis is very low. Three methods for improving the efficiency of alcoholysis are known: use of sub- and supercritical EH, use of transesterification catalyst and/or addition of some cosolvents [12].

The use of a cosolvent is a new way to accelerate the chemical reaction and it also improves reaction efficiency. The imidazole ionic liquid assisted in the process of PET alcoholysis with EH, as a cosolvent in obtaining DOTP. This process was catalyzed by the addition of 1.2% (w/w) of zinc acetate. The yield of DOTP reached 93% at reflux temperature and a reaction time of 5 h, while the weight ratio of the ionic liquid:EH:PET was 2:2:1. The reaction time of traditional reflux temperature alcoholysis of PET without ionic liquid as a cosolvent should be at least 10 h.

Oligoester plasticizers, with hydroxyl end-groups and an average molecular mass of 2500 g/mol, were also obtained by the degradation of PET waste by polyethylene glycol 400 and adipic acid in the presence of a transesterification catalyst. These compounds were tested as plasticizers in a poly(vinyl acetate) dispersion adhesives for flooring applications. The samples containing synthesized plasticizers were more flexible and had a higher thermal stability in comparison to commercial plasticizer 1,2,3-triacetoxypropane [13].

In recent years, the following compounds have been used as catalysts for the glycolysis or transesterification of PET: metal acetates [7,14], phosphates [15], solid super-acid, metal oxide [16,17], carbonate [18], sulfate [19] and ionic liquids.

In chemical synthesis organotin compounds are used expecially in the esterification and transesterification reactions of mono- and polyesters. Organotin compounds such as butylstannoic acid are used as catalyst to reduce the formation of unwanted by-products and also provide the required colour properties [20].

The aim of the presented work was the full replacement of the low molecular weight toxic phthalate-based plasticizers for PVC, which have been used so far, with environmentally friendly materials. The paper presents a new, previously unexplored method for obtaining oligomeric plasticizers in a reaction of PET waste transesterification by means of oligoesters.

2. Experimental

2.1. Materials

A sample of PET flakes was acquired from Industrie Maurizio Peruzzo POLOWAT Sp. z o.o. (average molecular weight 50 000 g/mol). Anhydrous 2-ethylhexanol, adipic acid (Ad), azelaic acid (Az), diethylene glycol (DE), dipropylene glycol (DP), 1.4-butandiol (BD), triethylene glycol (TE) and glycerine (Gl) were purchased from Brenntag Polska. All reagents were used as purchased without further purification. Fascat 4100, butylstannoic acid, was used as a catalyst.

2.2. Transesterification of PET

Waste PET-based plasticizer synthesis was conducted in two stages. A 1000 ml glass reactor equipped with an agitator, a splash-head, a thermometer and an azeotropic cap was filled with dicarboxylic acid, glycol and monohydroxyl alcohol (Table 2). The reaction was carried out in a temperature range of 140–160 °C under atmospheric pressure. The reaction was carried out until an acid value of less than 10 mgKOH/g was achieved. PET waste and 0.06% w/w of the Fascat 4100 esterification catalyst was added *in situ* to the oligoester obtained. The temperature of the reaction was increased to 190–210 °C. The total time of the synthesis was 10–12 h (Table 3).

The following plasticizers were obtained in the oligoester degradation of PET waste:

- azelaic acid with diethylene glycol and a 2-ethylhexanol end-group (designated as PETDEAz);
- adipic acid with dipropylene glycol and a 2-ethylhexanol end-group (designated as PETDPAd);
- azelaic acid with dipropylene glycol and a 2-ethylhexanol end-group (designated as PETDPAz);
- adipic acid with 1.4-butanediol and a 2-ethylhexanol end-group (designated as PETBDAd);

Table 2
Components used for the synthesis of plasticizers[a].

Symbol composition	PETD EAz	PETD PAd	PETD PAz	PETB DAd	PETB DAz	PETD PAdGl	PETD PAzGl	PETD EAzGl
PET (g)	30.20	31.61	28.90	34.08	31.00	24.64	22.24	23.00
2-ethylhexanol (g)	13.70	14.27	13.10	15.39	13.99	16.69	15.07	15.58
Adipic acid (g)	–	32.05	–	34.55	–	37.52	–	–
Azelaic acid (g)	39.40	–	37.80	–	40.47	–	43.59	45.05
Glycerine (g)	–	–	–	–	–	3.94	3.55	3.67
Dipropylene glycol (g)	–	22.06	20.20	–	–	17.22	15.54	–
Diethylene glycol (g)	16.70	–	–	–	–	–	–	12.70
1.4-butanediol (g)	–	–	–	15.98	14.53	–	–	–

[a] The reactant amounts provided have been calculated per 100 g of reactant load.

Table 3
The results of a gel chromatography analysis of the plasticizers obtained.

Symbol	Number average molecular weight M_n (g/mol)	Weight average molecular weight M_w (g/mol)	Dispersity
PETDEAz	1430	2500	1.75
PETDPAd	1530	2780	1.82
PETDPAz	1420	2600	1.83
PETBDAd	1610	2730	1.70
PETBDAz	1900	3400	1.80
PETDPAdGl	1590	3830	2.41
PETDPAzGl	1650	3950	2.39
PETDEAzGl	1670	3920	2.34
PETTEAd	1520	2780	1.83
H-1	2270	4230	1.87