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New Trends in Chemical Recycling of Poly(ethylene Terephthalate)

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Abstract: Chemical recycling of poly(ethylene terephthalate) (PET) by nonconventional transesterification and ammonolysis/aminolysis methods are discussed on the basis of literature and own experimental data. The obtained products of deep PET degradation using allylamine (*N,N'*–diallylterephthaldiamide), triethanolamine and other alkanolamines were prepared and characterized by DSC and elemental analysis.

INTRODUCTION

Chemical recycling, applied to postconsumer condensation polymers, which are very vulnerable to solvolytic chain cleavage, might be of great interest. Poly(ethylene terephthalate) (PET) is a packaging material widely used for the production of soft drink bottles and jars. This polymer does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream, it is seen as a noxious material.

Some of the important advantages of PET chemical recycling is the availability of a wide spectrum of degrading agents and of a great variety of potential products, such as monomers for polymer and resin syntheses or additives for polymeric materials (Ref. 1). Therefore in recent years, a growing interest has been observed in the use of PET waste for the production of specialized products, such as saturated and unsaturated polyesters, polyurethanes, coating materials and additives (Ref. 1).

Besides conventional degrading chemical agents such as methanol (methanolysis), mineral acids, alkalis, water or steam (hydrolysis) and glycols (glycolysis), an increasing tendency to use less common chemicals for PET degradation is observed.

Some new trends in the chemical recycling of poly(ethylene terephthalate) using nonconventional degradative transesterification and ammonolysis/aminolysis methods are discussed in this paper, both on the basis of literature and own experimental data.

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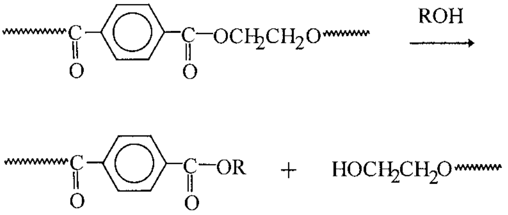
Degradative transesterification

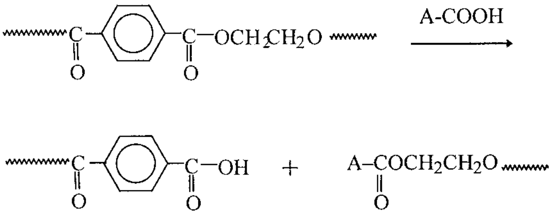
The degradative reactions of PET in the presence of alcohols, carboxylic acids or their esters take place in accordance with the following scheme:

– alcoholysis



(1)

– acidolysis



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The simplest examples of the degradative transesterification of PET are the reactions between long-chain aliphatic alcohols and the waste polymer (Refs. 2-5). The products obtained serve as plasticizers of poly(vinyl chloride) (PVC). Most often, PET degradation for the purpose of obtaining the so-called dioctyl terephthalate (DOTP), is carried out using 2-ethylhexanol (Refs. 2-4). The actual product is a mixture of DOTP and small amounts of 2-ethylhexyl 2-hydroxyethyl terephthalate and terephthalate oligoesters (Ref. 4). The plasticizer obtained in this way is at least as good as commercial DOTP from direct synthesis (Ref. 3) and can replace the most commonly used dioctyl phthalate (Ref. 3,4). Bathe (Ref. 5) described a way of obtaining a PVC plasticizer in a reaction of waste PET with poly(ester-ether) synthesized from trimellitic acid, C12 – C18 fatty acids and a mixture of diethylene glycol and ethylene glycol oligomers.

The degradative glycolysis PET is widely used on an industrial scale as a source of polyol components for the synthesis of unsaturated polyester resins and polyurethane or polyisocyanurate foams (Ref. 1). Simple glycolysis as a chemical method of PET degradation may be presently regarded as a conventional recycling method for this polymer and as such is not a subject of interest in this article.

In recent years, numerous technologies have been developed based on the degradative transesterification of PET using the products of degradation in situ so as to obtain useful products, mainly for the coating industry. It often occurs that the products of these technologies are of competitive price compared with equivalent materials obtained by classical synthesis. In addition, technologies of this kind are often wasteless or the waste volume is reduced to a minimum and, not uncommonly, they are less complicated than the traditional technologies.

The first technologies to obtain coating materials using the PET degradative transesterification products were claimed about ten years ago (Ref. 6,7). The waste polymer was dissolved in the product of pentaerythritol reaction with fatty acids at temperatures of 200–300 °C (Ref. 6). The intermediate was esterified with polycarboxylic acids; the final product of a molecular weight of M_n 2000–8000, was dissolved in a mixture of organic solvents (xylene – butanol). The lacquer obtained was characteristic by its stability in storage and by giving a glossy coating after drying (Ref. 6).

Lacquers with electroinsulation properties were prepared by the reaction of PET with glycols and triols at 180-240 °C in the presence of a transesterification catalyst (Ref. 7). The synthesized polyester was dissolved in a mixture of aromatic solvents (tricresol – xylene), and the lacquer obtained was deposited on copper wire.

The product of transesterification of waste PET (or poly(butylene terephthalate), PBT) with alkanediol esters and dicarboxylic acids at 300 °C are low-melting polyesters which find application as adhesives or coating materials (Ref. 8). For instance, a mixture of waste PET and PBT was subjected to a reaction with the product of polycondensation of adipic acid and butane-1,4-diol at 280 °C. The polyester obtained was applied as a powder coating for steel plate using the fluidized bed technique at 350 °C. The coating exhibits excellent adhesion to the metal base.

In the patent description (Ref. 9), a hot-melt adhesive based on PET was claimed. It was designated for paper or aluminium and polyethylene foils. PET scraps were subjected to degradative transesterification using the product of the reaction of trimellitic anhydride and poly(ethylene glycol) at temperatures of 230–250 °C, under a pressure of 0.1–0.3 MPa.

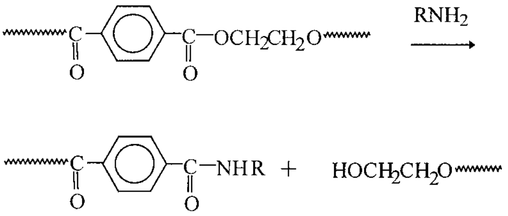
Pilati et al. (Ref. 10) have recently described the synthesis of alkyd resins for high-solid type paints, dried at room temperature, using waste PET. In the first stage, PET was subjected to degradation using trimethylolpropane and pentaerythritol at 230–240 °C, and in the next stage the product obtained underwent polycondensation with fatty acids. A high-solid paint was formulated on this basis consisting of 30–50 wt.-% of PET degradation products.

The waste PET was used as a component of alkyd resins for water-thinnable paints. The products from the reaction of the polymer with a mixture of fatty acids with high linoleic acid contents and trimethylolmethane were used in paints dispersible in water (Ref. 11).

Tosselli et al. (Ref. 12) have recently described the reaction of trimethylolpropane with waste PET at 230 °C using a mixture of intermediate oligomers for the synthesis of alkyd polyester with isophthalic acid, fatty acids and trimellitic anydride. The product was used for the formulation of a water-thinnable alkyd paint dried in air.

Ammonolysis and aminolysis

Both types of reactions cause PET degradation yielding amide derivatives.



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R=H (ammonolysis), alkyl (aminolysis)

Terephthaldiamide (TPDA) can be obtained as a product of the reaction of PET with anhydrous ammonia in ethylene glycol. This amide may be converted into terephthalonitrile, and further on into *p*-xylylenediamine or 1,4-bis(aminomethyl)cyclohexane (Ref. 13). The postconsumer PET was subjected to degradation with ammonia at a pressure of about 2 MPa, and in the temperature range 120–180 °C. The TPDA obtained has a purity of not less than 99 % and the yield is above 90 % (Ref. 13). A low-pressure method of PET ammonolysis with ammonia in ethylene glycol conducted at 70 °C with a catalyst is also known (Ref. 14). This method gives a TPDA yield of about 87 %.

The processes of partial, superficial aminolytic degradation of PET fibres have been subjected to numerous research studies (Refs. 15-22) and are practically applied on an industrial scale. Such modification processes improve the quality of fibre colouration and other technical and application parameters of the fibres.

From available literature it follows that in most cases the aminolytic modification processes of PET fibre surfaces are conducted using primary amines in aqueous solutions (Refs. 15-21) or less commonly, in the gas form (Ref. 21). The most frequently used degradative amines are methylamine (Refs. 16,18-20), ethylamine (Refs. 17,20), and butylamine (Refs. 20,21). Other amines used were ethanolamine (Ref. 20) and triethylenetetramine (Ref. 22). The purpose of the superficial aminolytic modification of PET was selective polymer degradation allowing control over its morphology. In conditions set in the aforementioned tests, the amorphous regions of a semicrystalline polymer undergo rapid degradation, whereas the crystalline regions are much more resistant to attack by amines (Ref. 15). Poppola put forward a mechanism of aminolytic degradation of PET based on the example of butylamine (Ref. 19).

Literature references concerning the deep aminolytic degradation of PET (or other polyesters) are very few (e.g., Ref. 23) and applications of the products of such a process on a commercial scale are unknown. Therefore, we have undertaken investigation on the aminolysis of the discussed polymer using amines and amino alcohols. Amines are organic bases causing cleavage of PET ester bonds faster than alcohols (glycols). In the first approach, the amine basicities can be evaluated using their ionization constant values. This enables the anticipation of the tendency of an amine to degrade the polymer. However, those parameters seem insufficient for determining the amino alcohol degradative ability.

EXPERIMENTAL

Materials

The degradative agents used were allylamine (Fluka) and ethanolamines (mono-, di- and triethanolamine) obtained from NZPO Rokita S.A., Brzeg Dolny, Poland. PET produced by the Chemical Plant ELANA S.A. in Toruń, Poland (the 'bottle' polymer) or waste polymer from packaging (soft drink bottles) were used.

Methods

Chemical degradation of PET was conducted in a 100-ml laboratory stainless steel autoclave equipped with a mechanical impeller and an electronic system for temperature control. The products were isolated by washing out the excess of degrading agent (allylamine, ethanolamine, diethanolamine, or triethanolamine) and the ethylene glycol formed in the reaction with distilled water, isopropyl alcohol or methanol and by subsequent drying under reduced pressure at about 85 °C. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer DSC-7 apparatus. Nitrogen was determined by the Kjeldahl method.

RESULTS AND DISCUSSION

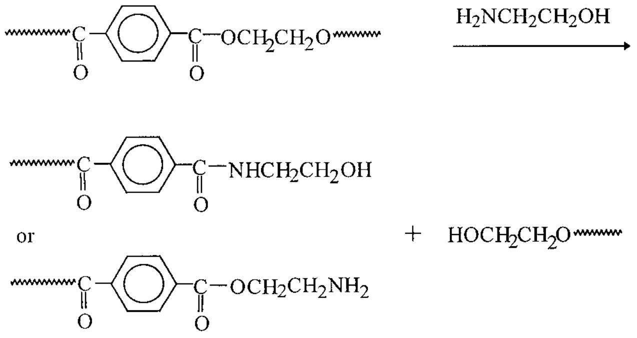
With the aim of obtaining products with an application value, we treated PET with several amines.

Degradation with allylamine

The degradation occurred at temperatures not higher than 180 °C, under a pressure of 1.5–2.0 MPa, without any catalyst (Ref. 24). After removing ethylene glycol, a high-purity powdery product was obtained. Its melting point (220 °C), as determined by DSC, correlates well with the range of melting temperature (217-220 °C) of *N,N'*-diallylterephthaldiamide obtained by synthesis (Ref. 25). The presence of virtually a single chemical compound was confirmed by ^{1}H NMR (Ref. 24). The diamide obtained is of interest as a high-temperature solid crosslinking agent.

Degradation with ethanolamines

The degradation with mono- and diethanolamines may occur by the transesterification–aminolytic mechanism, i.e., as a result of the cleavage of PET ester bonds; new ester or amide bonds are formed. However, the degradation of the polymer with triethanolamine gives ester products.



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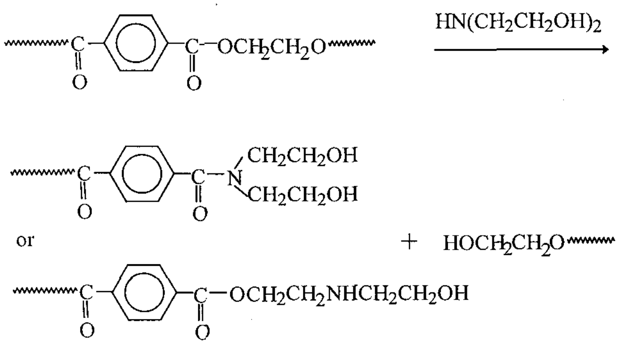
As a result of deep PET degradation with ethanolamines, one may obtain a defined polyol comprising four hydroxy groups (with triethanolamine) or mixtures of amidoesters (with mono- or diethanolamine). Table 1 shows that the product of deep PET degradation with triethanolamine, after washing out ethylene glycol with methanol, comprises virtually a single chemical compound with a melting temperature of about 191 °C. The DSC analysis allowed the identification of the presence of two main components in the products of PET degradation with monoethanolamine (melting temperatures of about 201 and 234 °C; Table 1). A higher-melting compound is *N,N'*-di(2-hydroxyethyl)terephthaldiamide (Refs. 23, 26). The lower-melting compound is identified as the mixed amide-ester of terephthalic acid. In the products of PET degradation with diethanolamine, DSC thermograms show the presence of several chemical substances.



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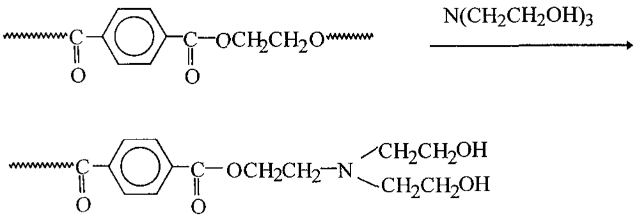

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Taking into consideration the presence of functional hydroxy and amine groups, the products of deep PET degradation with ethanolamines may constitute potentially interesting raw materials for the synthesis of polyurethanes, mainly rigid polyurethane foams. The research on the PET degradation with amines, amino alcohols and on their application is continued.

Table 1. Characteristics of the products obtained by chemical degradation of PET with ethanolamines

Characteristics	Monoethanolamine	Diethanolamine	Triethanolamine
Nitrogen content (wt.-%)	10.95	6.85	–
Theoretical nitrogen content [a] (wt.-%)	11.1	8.23	6.53
DSC melting temperature (°C)	201, 234	154, 210-225	191

[a] in deep-degradation product

CONCLUSIONS

Chemical recycling of poly(ethylene terephthalate) creates wide possibilities for waste polymer utilization in the manufacture of intermediates used in the synthesis of useful polymers, resins and additives. Possibilities of deep PET degradation were examined. The defined and potentially useful substances can be obtained by the polymer chain cleavage with allylamine or ethanolamines, in particular triethanolamine.

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