

Complex Utilization of Polyethyleneterephthalate Wastes

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INTRODUCTION

Utilization of items made of polyethyleneterephthalate (PET) wastes is now one of the most important ecological problems. Waste bottles are considered to be the main items to be utilized. PET bottle chips have emerged as one of the most popular among these items.

The global production capacity of PET bottle chips increased from 1.6mn tons in 1990 to 8.5mn tons in 2000. North America (35.9%) Asia (34.3%) and Europe (21.8%) are the leader regions of PET bottle chips production.

Currently only about 3.5% of all plastics generated is recycled, compared to 34% of paper, 22% of glass and 30% of metals.

The solution of utilization of post-consumer PET bottles is connected with various difficulties among which we can underline the followings:

- the collection of these articles which is determined, in particular, by their low weight (weight of a bottle is only tens of grams). This leads to the low profitability of the majority of the existing processes.
- the instability of markets for recovered material
- the lack of collection infrastructure
- the contamination of collected bottles. Markets for colored PET material are more limited than those for colorless PET, hence collection schemes may limit the range of PET bottles recovered to clear, light blue tint and black bottles.
- existing product specifications can exclude use of recyclate PET in some applications where recycled materials may be able to match, or exceed, technical performance requirements.

PET UTILIZATION

Recycling PET is similar to the polyethylenes (PE). Bottles may be color sorted and are ground up and washed. Unlike polyethylene, PET sinks in the wash water while the plastic caps and labels are floated off. The clean flake is dried and often repelletized.

Recycled PET has many uses and well established market for this useful resin. The largest usage is in textiles and fibers. PET bottle recyclate can be used also in packaging: manufacturing of food and non-food containers; strapping - PET is the strongest of the plastic alternatives to steel, but is more expensive, which has limited its use in mass applications and restricted its use to those applications where strength is essential. Chemical recycling is another established method

for recovering reclaimed post-consumer waste. This involves the break down of the PET flake chemically into chemical precursors, which are then made available for re-polymerization or other chemical processes. However, equipment costs being high, it requires large turnovers to be economically available..

The various chemical recycling techniques are: glycolysis, methanolysis, hydrolysis, saponification and pyrolysis. The selection of the appropriate process depends on the quality of the reclaimed input material. For example, glycolysis and methanolysis are unable to remove colours added to PET feedstreams during their original formulation. These therefore require additional purification.

The chemical methods of post-consumer PET are perspective ones. The main advantage of these methods, on the comparison in particular with the already implied processes (URCC, developed by Cleanaway Deutschland and Frauenfeld plant in Switzerland, for example) is in the effect unlimited necessity of the end products, as TA, or its dimethyl ether may be used as initial components for the polymerization of PET, and consequently they can be used for the production of food containers (bottles, canisters, etc.), quantity of which is calculated by millions of items per year and has steady tendency toward significant increase.

EXPERIMENTAL RESULTS:

Hereinafter our investigations are illustrated.

As a main method we use the thermo-vaporous and hydro-thermal methods, i.e. treatment of items in a water vapor or in a liquid phase in autoclave at high pressure and temperature (180-220⁰C).

The special feature of the created technology was the possibility to use articles made of PET without preliminary cleaning and without also the removal of polyethylene component of the bottles. Under laboratory conditions the process was carried out in 5 liters autoclaves; in the industrial conditions the autoclaves of the building material plants, such as silicate brick, as well as cellulose and water glass, can be used. The volume of building construction autoclaves can reach 30m³, where as those of paper industry grows to 300 m³. In the majority of the cases the heating of autoclaves is achieved by using overheated vapor, so the power expenses are low.

With a target towards realization of a general utilization problem of PET wastes the following processes were investigated in our work:

1. re-crystallization of synthesized TA;
2. TA interaction with an ammonium hydroxide solution at normal conditions;
3. TA structural changes upon its treatment in autoclave at various temperatures.

PET Autoclaving in Neutral Media

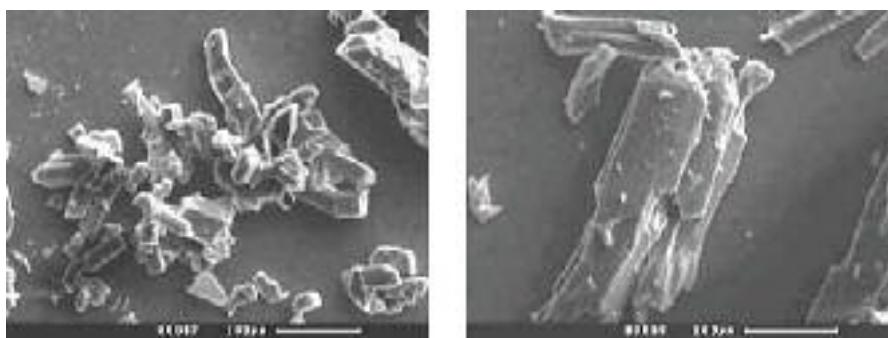
During treatment of used PET wastes in autoclave in neutral media a complete or partial decomposition of the initial substances to its consisting components takes place. Besides, a variety of intermediate substances, probably different esters, are also notified [1]. This process allows us to obtain from used PET items products, which are well soluble in alkaline media under normal conditions. As a consequence soluble derivatives of terephthalic acid are formed. A further neutralization by solutions of mineral acids leads to the formation of TA. The status of crystallization mechanism of TA remains here unclear. We notified that, under these conditions, an amorphous, or fine-crystalline mass, is formed.

PET Autoclaving in Acidic Media

The decomposition of PET, resulting as a treatment in the autoclave in acidic media, allows the direct formation large crystals of TA (tens of microns), which increases the perspectives of this process as a method of utilization of PET wastes. Investigation of both structural transformations TA and the process of TA re-crystallization is necessary to obtain TA in a more convenient form for further usage. We can notice that teflon is the most suitable material for containers with acidic media.

According to our opinion the most interesting in this process is the decomposition of PET wastes into its initial components - TA and EG – upon treatment in autoclave in solutions of mineral acids at 200°C. At these conditions TA, as we mentioned above, large crystals are formed (Fig. 1). The degree of TA purity, according to NMR spectra comparison was identical to TA of special purity mark, available in the market. Another result, received by the autoclave treatment of PET items, was the re-crystallization of TA. Commercial TA represents a disorder substance with crystals size about 10 μ . In the process of PET synthesis (polycondensation of TA and EG), size of TA crystals may be quite significant factor. The larger crystal size means the higher is the purity of TA.

Nevertheless we have to notice that aggressive acidic media require special resistant materials for the containers, and this fact leads to a considerable increasing of the equipment coasts.



*Fig. 1 - Electron microscopic photos of a- crystals of initial TA
b- crystals of TA treated at 300°C for 16 hrs.*

PET Autoclaving in Basic Media

Basic media are achieved by introducing ammonium hydroxide, or solutions of hydroxides of alkaline elements, or urea to the reaction. Various containers, including metallic ones can be used here. The resultant of the autoclave treatment in alkaline media is the formation of terephthalates. These salts, as we shall demonstrate later, are used in different interesting fields. The subsequent precipitation of TA from terephthalates by solutions of mineral acid is an aspect as it leads to the formation of an acid of high purity.

Nitric acid appears to be, from the technical point of view, the most acceptable, since it enables the process to be carry out obtaining TA practically without withdrawals (ammonium nitrate it is a good fertilizer). In Fig. 2 we represent electronic microphotography of the crystals of TA obtained by neutralizing the solution of ammonium terephthalate using hydrochloric acid (Fig. 2 b) and the commercial TA used in the polymerization of PET (Fig. 2 a) .

As can be seen from these photos the size and form of crystals in both cases are practically identical. The proposed method exclude the possibility of formation of organic impurities, such as toluenic acids, which are not appreciable in PET production. NMR results confirm this fact. Our investigations made it possible to develop the method of obtaining TA with the intended size of crystals. Method based on the treatment of initial TA in the autoclave in the vapors of water at temperatures in the range of 150-400⁰C, enable us to increase the size of crystals up to hundreds of microns. (Fig. 2 c)

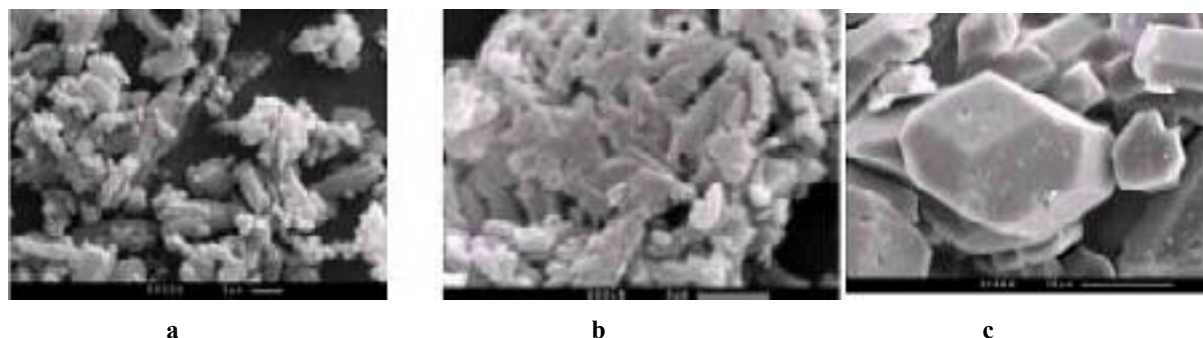


Fig. 2 - Electron microscopic photos of
a- Initial TA; b- TA, obtained from ammonium terephthalate and HCl;
c- TA after autoclave treatment at 200⁰C for 120 hrs

TEREPHTHALATES AS CONSEQUENT PRODUCTS

The synthesis of various terephthalates in one of the interesting aspects of the further using of the products of decomposition of PET we manage to obtain ammonium terephthalate as well as terephthalates of elements of Groups I-IV.

TA derivatives are rather interesting products, and, in particular, TA ammoniac salts. The salts of TA and bivalent copper absorb oxygen, nitrogen, argon and xenon up to two moles of gas/1 mole of salt.

Ammonium terephthalate

Ammonium terephthalate can be obtained directly in the autoclave by treating post-consumer PET at 200⁰C in the presence of NH₄OH and subsequent its excretion in the solid state. Heating to 150⁰C leads to evaporation of ammonia, although the structure of ammonium terephthalate remains the same up to a content of nitrogen equal to 3.48 wt.%. This allows us to consider ammonium salt as the compound of variable composition with general formula (NH₄)_xH_{2-x}(OOC₆H₄COO); x = 1.7±0.4 [2]. This structure is formed when part of ammonium ions are not present, and the molecule is ready to accept other compounds to be absorbed in its structure, which enables such a salt to be used as the selective absorber, molecular sieve, etc. [3]

Terephthalates of Group I-II

Obtained ammonium terephthalate is used further as an initial compound for synthesis of terephthalates of Groups I and II. The last were obtained by their precipitation from the reaction of ammonium solution of ammonium terephthalate with the solutions of salts of these elements. Precipitation of terephthalates of alkali metals (K, Na) was conducted in an excess of ammonium hydroxide. This fact does not prevent the formation of salts because of the high solubility of

hydroxides of alkali metals under these conditions [4]. With the conduction of terephthalates of Group II (Mg, Ca) relatively insoluble hydroxides are formed. These hydroxides interfere with terephthalates and this fact leads to considerable difficulties to obtain pure salts. Therefore the ammonium solution of ammonium terephthalate should be first neutralized by solution of HCl up to pH = 6 and then introduced for the substitution reaction.

For Na both mono- and di-substituted terephthalates salts were obtained, where as for potassium only monosubstituted salt is formed [5]. Individual diffractograms were obtained for each terephthalate. Upon heating different terephthalates behave themselves similarly: endothermic effects, related to the loss of crystallization water (where it is present), and exo-effects, one of them is noticed at temperature higher than 500⁰C and related with the process of decomposition of terephthalates. Further thermo-oxidizing destruction leads to the formation of carbonates, which are transformed at temperatures above 800⁰C into oxides (Na₂O, K₂O, CaO, MgO). Only for di-substituted sodium terephthalate the end product is sodium carbonate.

Aluminum Terephthalate

In the case of aluminum terephthalate the use of above mentioned method leads to the formation of amorphous compound.

To obtain crystalline aluminum terephthalate (Fig. 3) hydrothermal method was applied. TA (both commercial and obtained from post-consumer PET) and a solution of aluminum chloride were introduced into steel or quartz container, which was placed in the autoclave. The TA:Al ratio varied in the range 1.6÷2.4. In all cases crystals of aluminum terephthalates with the following formula Al₂(C₆H₄(COO)₂)₃·2H₂O (chemical element analysis confirm the presented formula).

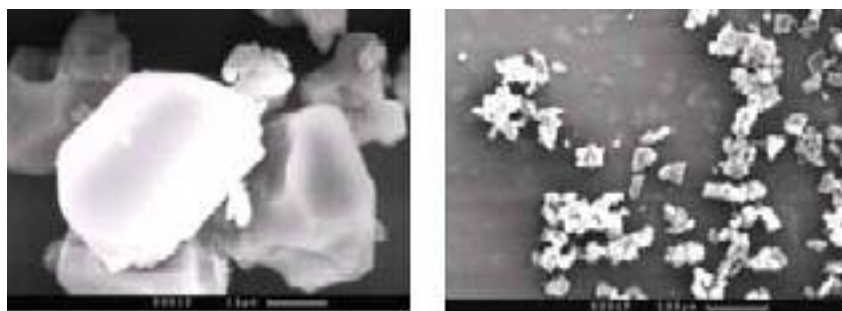


Fig. 3 - Electron microscopic photos of aluminum terephthalate

Values of interplanar spacing for aluminum terephthalate from X-ray phase analysis are represented in Table 1.

Table 1- Interlayer distance (d, Å) and intensity (I, %) of aluminum terephthalate crystals (X-ray phase analysis data)

d, Å	8,59	5,79	4,98	4,17	3,68	3,30	2,84	2,76	2,21
I, %	76	54	100	76	68	79	34	14	14

Thermo-gravimetric analysis shows here two exo-effects typical for terephthalates at 550⁰C (related with oxidizing thermal destruction of organic ligand) and 730⁰C (combustion of organic residue). Intensive loss of weight reaches 85% at 730⁰C. X-ray analysis of the product obtained after heating to 950⁰C shows the presence of wide reflexes, corresponding to γ -Al₂O₃.

IR spectra of aluminum terephthalate, obtained in the autoclave, and of the samples thoroughly heated at 500, 600, 900⁰C shows, that the valence vibrations of CO, CH, CC, OH, AlO bonds partially keep existing after treating at 500⁰C. The valence vibrations of OH group (ν_{OH}) in the initial product has two strips at 3609 and 3443 cm⁻¹ but only one at 3420 cm⁻¹ after treatment at 600⁰C. Besides a deformation vibration of water molecule (δ_{HOH}) at 1631 cm⁻¹ remains in the spectrum even after treatment at 900⁰C. The presence of this vibration is caused, probably, by the process of polycondensation. During the decomposition aluminum terephthalate upon thermal treatment Al(OH)₃ is formed. Further heating of aluminum hydroxide leads to the disappearance of structural water and to the formation of γ -Al₂O₃.

CONCLUSIONS:

Different aspects of utilization of post-consumer PET demonstrates a complex approach of solution of one of the most actual and urgent ecological problems in the present time. Obtained materials can meet wide practical application. In particular, their layered structure with fixed interlayer distances makes them suitable to be used as absorbers and molecular sieves. The chemical compound and structure of these salts is in favor of their usage as filler for various plastics. Also it is quiet interesting to expose terephthalates to thermal treatment at high temperature to obtain corresponding oxides in fine crystalline form. During this work we obtained fine-grained oxides of calcium, magnesium and aluminum, which can find wide application. Besides an important aspect remains the decomposition of PET to its consisting components as well as its transformation to powder and further using of post-consumer PET in manufacturing various building materials. Fine-crystalline oxides CaO, MgO with the particle size of 5-300 microns can be used for manufacturing special ceramics, fire-proof materials. Sub-micron particles of Al₂O₃ may represent special interest and perspective applications.

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