Processing of new materials using thermal and thermo-vaporous treatment of terephthalates

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Abstract: Utilization of used polyethyleneterephthalate (PET) is now one of the most important ecological problems. Its solution is related mainly with various difficulties. The solution of this problem seems to be in the creation of remunerative processes, for which post-consumer PET is used as a source material. Were developed several highly profitable processes of utilization of PET articles. Keywords: PET, utilization, autoclaving, terephthalates

Polyethylene terephthalate (PET) is widely used in the production of packing material - bottles, containers, film and others. Because of the large volume of production (up to 5 millions tones per year) vital problem is the recycling of the articles made of the PET used. Basic difficulty in this case is, in particular, the collection of post-consumer bottles, since the weight of a bottle does not exceed, usually, 50 g. Collection of the post-consumer bottles sufficiently labor-consuming and expensive process. Taking into account the preliminary preparation of the used articles (washing, drying), the cost of source material for the recycling becomes so high that the majority of the processes of recycling turns unprofitable. Therefore immediate is the development of the highly remunerative processes of the utilization of the articles made of the post-consumer PET.

The present work represents some developed highly remunerative methods of the utilization of the post-consumer PET articles. In our opinion, the following processes are most promising:
1. Production of comparatively expensive and claimed articles made from post-consumer PET.
2. Decomposition of PET into the monomers - separately clean terephthalic acid (TA) and the ethylene glycol (EG)
3. Obtainment of various terephthalates and their use for the production of advantageous products and in different technological processes.

The production of articles made of the post-consumer PET is the now most widespread process of its utilization. By Basic difficulty here is related to the prohibition in the legislation of the majority of the countries concerning the use of post-consumer PET for the production of food containers (bottle-to-bottle production), and also the high prime cost of source material. The nonfood market for articles made of post-consumer PET is sufficiently limited. This fact substantially hampers the creation of the highly remunerative processes of PET utilization by this method. We developed the process of the transfer of post-consumer PET into the brittle state. Process consists in treatment of post-consumer PET in the autoclave at a temperature of about 200°C. PET converts to crystalline state, it becomes brittle and it can be crushed to the size of the particles of several microns. This material can be used as filler for epoxy and polyester resins, for creating of epoxy and polyester paints and puttyings, and also be used as the source material for the process of decomposition of PET into its initial components. Figure 1 shows that, in spite of differences in X-ray diffraction patterns of the PET films (fragments of bottle) before and after autoclave treatment of amorphous and crystalline, the crystallization of polymer occurs without decomposition of PET.
Earlier [1] were developed the processes of decomposition of the used articles made of amorphous PET into the monomers by their treatment in the autoclave in solutions at temperatures of about 200°C in acidic (HCl), neutral (H$_2$O) and alkaline (NaOH) media. The use of crystalline PET makes it possible to reduce the temperature of autoclave treatment to 100-120°C. Reaction medium can be the solution of ammonium hydroxide, in which amorphous PET does not dissolve even at 200°C. For the realization of this process widespread autoclaves, which can function to pressures up to 0.5 MPa, can be used. From the obtained solution of ammonium terephthalate after the addition of nitric acid crystals of TA with the size in the range of 1-5 microns precipitate. To obtain pure terephthalic acid it is necessary to recrystallize TA by dissolving it in solution of ammonium hydroxide and, subsequently, precipitating it by mineral acid. The practical absence of a waste is a special feature of this process, as ammonium nitrate obtained after the precipitation of TA is a component of mineral fertilizers. The proposed process makes it possible to obtain TA without organic impurities. This fact is confirmed, in particular, by the results of NMR-spectroscopy studies. Figure 3 presents the NMR spectra of vendible pure terephthalic acid (production of “Merk Schuchardt OHG” and of samples of TA obtained after the dissolution of the crystalline used bottles in 5% solution of ammonium hydroxide with subsequent precipitation by nitric acid. The NMR spectra of $^{13}$C were obtained on “Bruker AC -200” spectrometer. The identity of spectra indicates the absence of organic impurities.
The quality of terephthalic acid, besides contaminant composition is qualified by size of TA crystals. The industrial terephthalic acid, which is used for the production of food containers has a size of crystals of about one micron. This acid is not entirely convenient for other technological processes, in particular, for obtaining polyester resin, where it is desirable to have a size of crystals on the order of 50 microns. At the same time, TA produced, for example, by “Merck Schuchardt OHG” has size of crystals in the range 50-150 microns. In our work the processes of agglomeration of TA crystals were regarded.

According to measured impurity contents in various TA samples (see Table) the obtained terephthalic acid not only analogous to the pure one produced by “Merck Schuchardt OHG”, but also from many parameters, even it exceeds the “Merck” one.

|   | Na  | K   | Ca  | Mg  | Fe  | Si  |
|---|-----|-----|-----|-----|-----|-----|
| 1 | 0.0040 | 0.0014 | 0.0022 | 0.0040 | 0.0002 | 0.0360 |
| 2 | 0.0860 | 0.0015 | 0.0106 | <0.0002 | 0.0200 |
| 3 | 0.0042 | 0.0009 | 0.0124 | 0.0004 | <0.0002 | 0.0012 |

1) Acid produced by “Merck Schuchardt OHG” Germany.
2) Acid obtained under laboratory conditions from the hydrolysis of PET in 5% alkaline solution.
3) Acid obtained under laboratory conditions from the hydrolysis of PET in 5% alkaline solution, recrystallized from ammonium hydroxide solution.

To increase the size of TA crystals two processes were developed:
1. Autoclave treatment of TA obtained immediately after precipitation from ammonium terephthalate solution by mineral acids. The optimal parameters of autoclave treatment were determined. It is shown that the treatment of initial TA in the autoclave in the vapors of water at 200°C makes it possible to increase the size of crystals to 50 microns.
2. Flocculation is a more promising method. It is shown that TA in the aqueous solutions of some salts flocculates, in this case an increase in the size of flocculi to 1000 microns is observed. The selection of flocculant makes it possible to obtain TA in a narrow range of the sizes of crystals. The utilized salts then are completely moved by washing of final crystals using solutions of mineral acids. The structure of flocculi in this case is not disrupted.

The obtained results make it possible to recommend the process of recycling the post-consumer PET for obtaining the pure TA, which can be used both in the production of food containers and in the production of polyester resins.
The realization of the process of ammonium terephthalate synthesis from the PET post-consumer articles makes it possible to obtain, practically, unlimited source of raw material for obtaining terephthalates - salts of TA. Earlier we developed the synthesis of ammonium terephthalate and terephthalates of II, III groups and their corresponding oxides, which are formed by thermal decomposition of terephthalates [2,3,4]. Most interesting is the use of terephthalates for obtaining nanocrystals of aluminum and zirconium oxides. The interaction of ammonium terephthalate with fine-crystalline aluminum (Zr) hydroxide leads to the formation of crystalline supramolecular structures representing ammonium terephthalate, which contains amorphous aluminum or zirconium hydroxides. With their thermal decomposition crystals of α-alumina or monoclinic zirconium oxide with size of crystals in the range of 50-100 nanometers are formed. These crystals can be used, in particular, for obtaining the ceramics (Fig.4).

Perspective is the use of salts of TA in different technological processes. It was shown that the use of solutions of terephthalates of potassium, sodium and ammonium, as activators in the process of thermovaporal treatment of aluminum hydroxide, makes it possible to obtain the fine-crystalline particles of corundum with the size of crystals up to 300 microns. Without the use of activators such crystals cannot be obtained. Corundum crystals successfully are used as the abrasive powders and for creating abrasive tools.

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