

PROCESS OF DESTRUCTION OF TEREPHTHALIC ACID IN SUPERCRITICAL WATER

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Terephthalic acid (TA) is one of the important technical compounds. It is used in large quantities in the synthesis of polyethyleneterephthate (PET) and different other organic productions such as the preparation of polyester resins. World production of TA reached millions of tons/year, and the tendency here is towards the growth. In many cases using of TA is determined by its properties, and in particular, the dimensions and form of its crystals, degree of its purity, etc. These properties are considerably modified by autoclave treatment of TA. It is interesting, in this occasion, to study the behavior of TA in contact with water fluid or vapor under critical or supercritical conditions.

Previously [1] we show that TA can be obtained from autoclave treatment of PET items. In many cases TA with extremely small particles is formed. The increasing of the size of these crystals is a separate problem which has to be solved. Re-crystallization using autoclave treatment was identified in paper [2].

In this study, a detailed investigation of the growth crystal process of TA in under- and supercritical intervals of water vapor pressure is carried out.

Commercial TA (purity +99%) obtained from “Acros Organics” and “Khimreativ” (Russia) was used as initial material. Autoclave treatment was carried out under different temperatures in the interval 150-450⁰C and in autoclaves of different volumes – 15 cm³, 1 l, 2.5 l. Obtained samples undergo X-ray diffraction analysis, IR spectroscopy, electron microscopy, chemical analysis.

Element composition of both initial and treated TA was investigated by gas chromatography method (CHNSO “E” Carlo Erba). The composition of the liquid phase, obtained from autoclave treatment of TA was determined on GLC: Pye Unicam 104 Column Ultra-1 (HP) 25 m x 0.2 mm x 0.33 microns (crosslinked polymethylsiloxane) with mass spectral identification of obtained products. Micro photos of crystals were obtained on electron microscope DRON-7 with copper cathode. IR Fourier spectrometer NEXUS (Nicollet) was used to carry on IR spectral analysis. Tablets of samples pressed with KBr were used for this sake.

The results of electron microscopy investigation of TA samples are demonstrated in Figures 1,2. Photos (A) in Figures 1,2 belong to crystals of initial TA from different manufacturers. These photos illustrate a considerable difference of the size and form of TA crystals. In photo (A) of Figure 1 acid has the form of regular crystals with diameter of 1-5 microns, where as crystals of TA in photo (A) of Figure 2 are much more large (50-150 microns) and they have irregular form, probably related with the method of manufacturing of TA in this case.

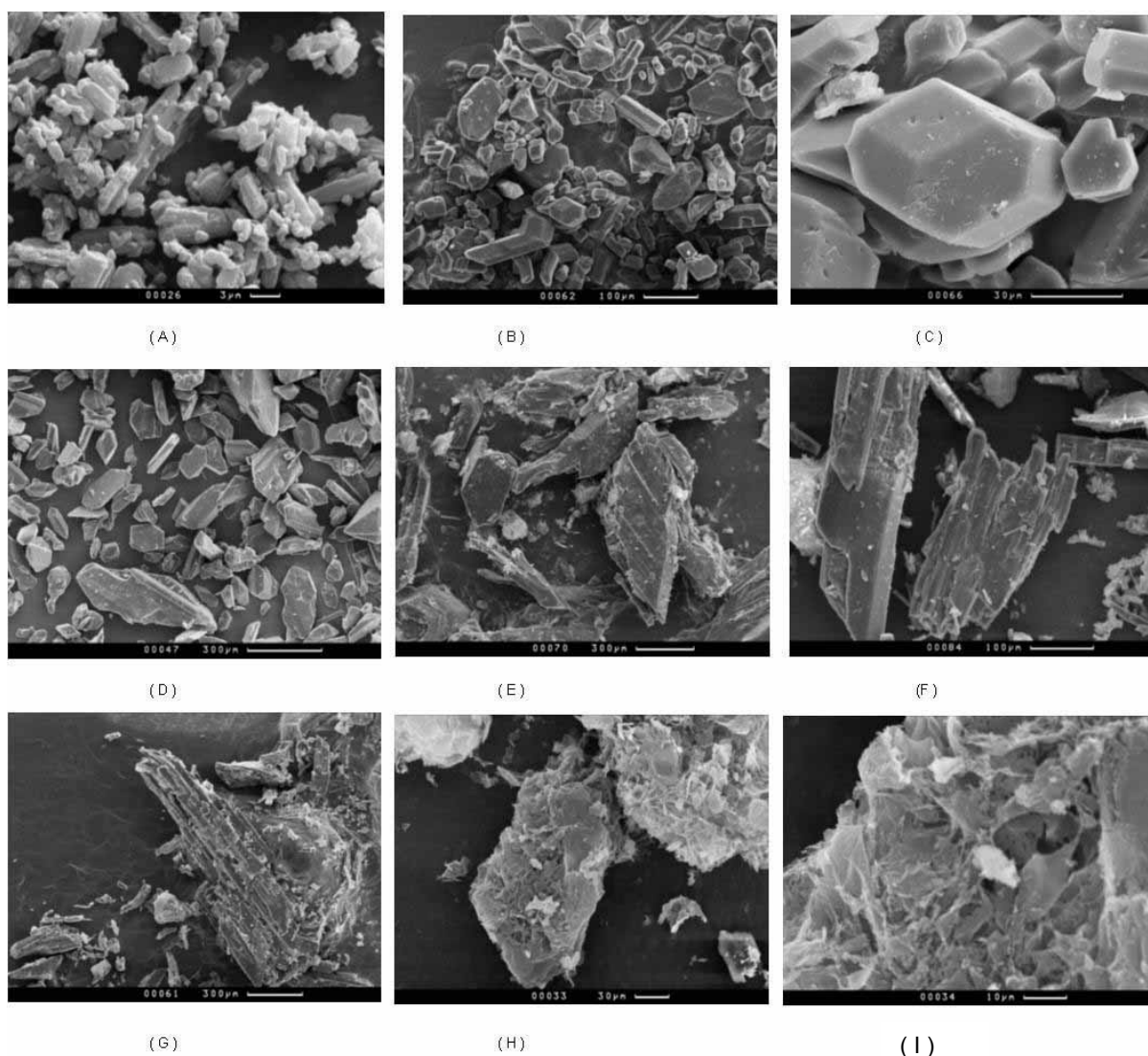


Figure 1 - Electron microscopy photos of TA (Khimreactiv): A- Initial TA; B,C- TA, autoclave treated, 200 °C, 96 hrs; D- TA, autoclave treated, 300 °C, 16 hrs; E- TA, autoclave treated, 350 °C, 16 hrs; F- TA, autoclave treated, 400 °C, 2 hrs; G- TA, autoclave treated, 400 °C, 96 hrs; H,I- TA, autoclave treated, 420 °C, 24 hrs.

Using for the study crystals of different size and form enabled us to determine the regularities of the influence of fluid and vapor water on the samples upon autoclave treatment.

In Figure 1 the electron microscopy photos of samples obtained from TA with smaller initial size crystals are demonstrated. As it is shown in these photos, autoclave treatment of TA at 200°C for 96 hrs leads to a considerable increase in the particle size (up to 300 microns). These crystals have regular forms and sharp edges. Treatment at 300-350°C leads to further increasing of crystal size, although crystals here have the shape of elongated particles consisting of plates of the same orientation. Autoclave treatment at 400°C leads to the disappearance of the borders between the plates and transformation of crystals to aggregates without a determined shape. Increasing the treatment temperature to 420°C leads to the formation of shapeless particles consisted of fiber-like interlace with porous structure.

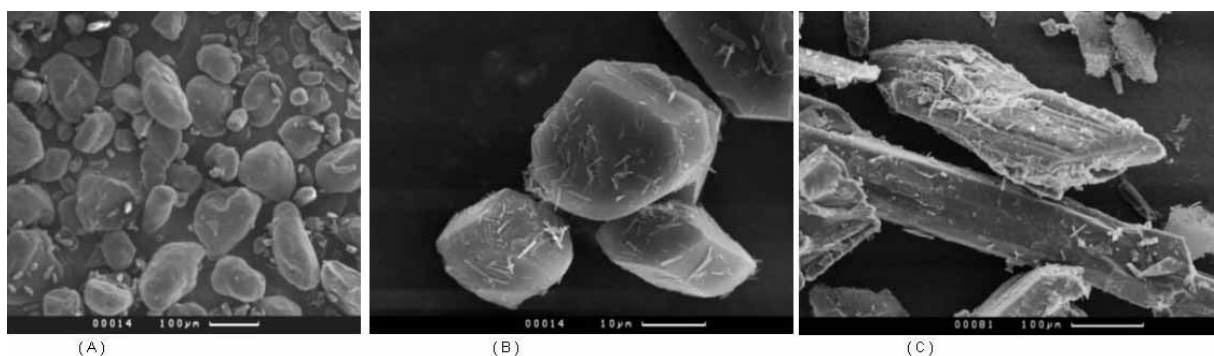


Figure 2 - Electron microscopy photos of TA (Acros Organics): A- Initial TA; B- TA, autoclave treated, 200⁰C, 24 hrs; C- TA, autoclave treated, 350⁰C, 15 hrs.

Figure 2 includes electron microscopic photos of samples obtained from TA manufactured by “Acros Organics”. As we mentioned above crystals of initial TA are essentially more large (D = 50-150 microns), but, nevertheless, transformation of these crystals upon autoclave treatment is similar to those illustrated in Fig. 1, although crystal size after treatment at 350⁰C is much bigger than for similar samples demonstrated in Fig.1, and the particle size may reach here some millimeters.

In Table 1 the results of element chemical analysis of autoclave treated TA samples are illustrated. Comparing here results for samples N 4 and 6, we can conclude that treatment at 400⁰C may lead to condensation of TA and to the formation of terephthalic anhydride.

Table 1 - Element chemical analysis of products of TA autoclave treatment and calculated values of element composition of some products

N	Sample, treatment conditions	Mass %		
		C	H	O (calculated by difference)
1	TA (Acros Organics) Autoclave treated 350 ⁰ C, 190 atm, 12 hrs	59.0	3.2	37.8
2	TA (Khimreaktiv) Autoclave treated 350 ⁰ C, 190 atm, 15 hrs	57.7	2.8	39.5
3	TA (Acros Organics) Autoclave treated 400 ⁰ C, 265 atm, 2 hrs	58.8	3.1	38.1
4	TA (Khimreaktiv) Autoclave treated 400 ⁰ C, 265 atm, 2 hrs	61.0	3.4	35.6
Calculated composition				
5	Terephthalic acid C ₈ H ₆ O ₄	57.83	3.61	38.56
6	Terephthalic anhydride C ₁₆ H ₁₀ O ₇	61.15	3.18	35.67

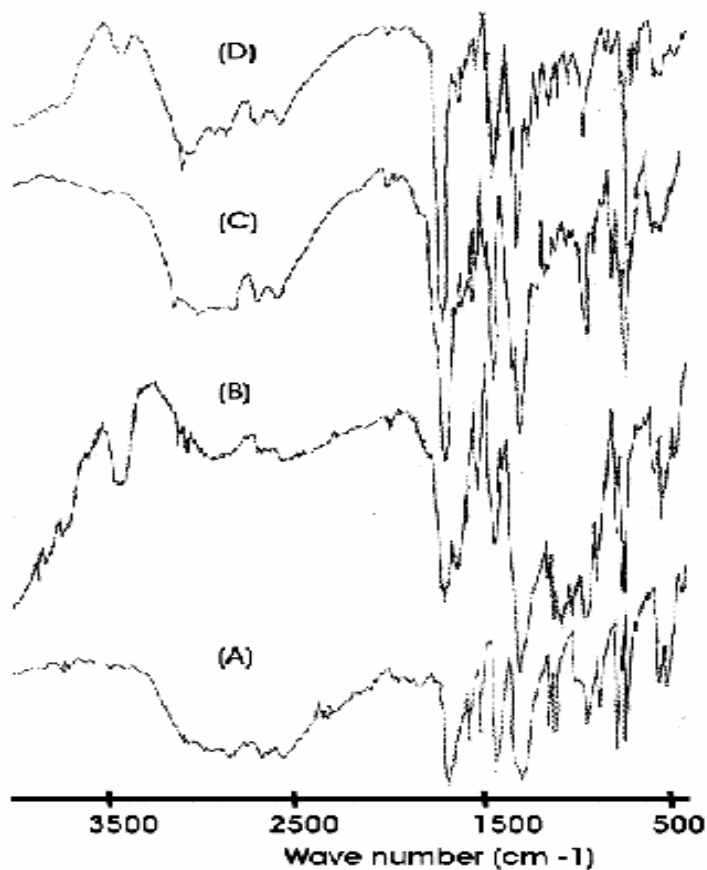


Figure 3 - IR-Spectra of:

- A- Initial TA**
- B- TA, autoclave treated, 200 °C, 24 hrs**
- C- TA, autoclave treated, 350 °C, 15 hrs**
- D- TA, autoclave treated, 400 °C, 2 hrs**

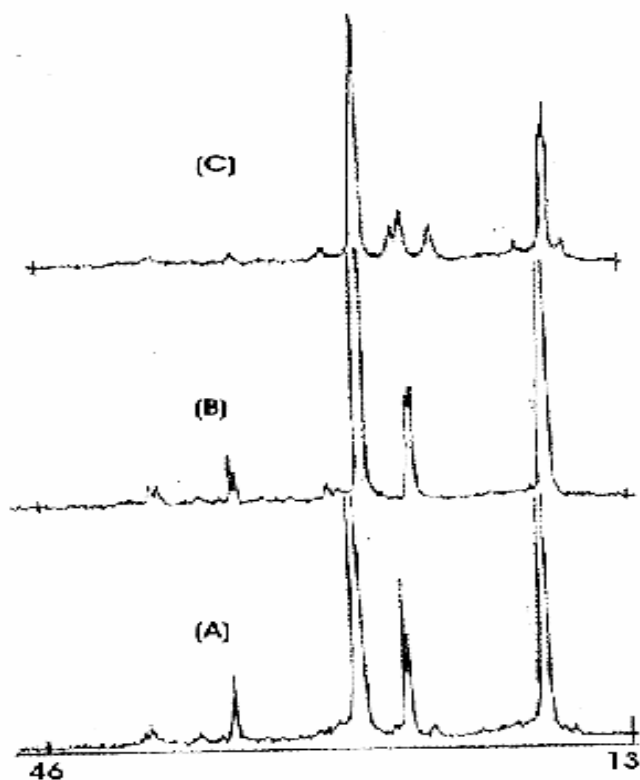


Figure 4 - X-ray diffraction patterns of :

- A- TA (Acros Organics) autoclave treated, 400 °C, 2 hrs**
- B- TA (Khimreactiv) autoclave treated, 200 °C, 24 hrs**
- C- TA (Khimreactiv) autoclave treated, 400 °C, 2 hrs**

IR spectra of some samples of TA treated in the autoclave at 350-400⁰C (Figure 3) illustrate a considerable decrease of absorption in the interval 1900-3100 cm⁻¹, and in some of them we can see a peak around 3420 cm⁻¹, accompanied by another peak at 1626 cm⁻¹. These absorption peaks may be related to valence and deformation vibration of water molecules, formed after dehydration of TA molecules as a result of their condensation. At the same time we can notice the presence of peaks at 810 and 708 cm⁻¹ belonging to the group (-C-O-C-) [3] and the disappearance of the peak at 730 cm⁻¹.

On Figure 4 we can see the X-ray diffraction (XRD) patterns of TA samples, treated in the autoclave at different temperatures. XDR patterns of TA, treated at 200⁰C are identical to those for initial terephthalic acid, where as for samples, treated at 400⁰C we can distinguish extra patterns corresponding to distances between layers equal to 5.47, 4.67 and 3.77 Å. The intensity of these patterns increases with the increasing of treatment time the autoclave.

An interesting fact is noticed when autoclave treatment is carried on at temperatures higher than 400⁰C. For example, as a result of autoclave treatment at 420⁰C we obtain a liquid phase with typical benzene smell. Chromatography analysis (Figure 5) shows the presence of three separate compounds, for each of which we can distinguish a corresponding peak. Further mass spectral analysis determines that:

- the first compound (peak at 3.19) is benzene (mass spectral line was distinguished at 78)
- the second one is benzoic acid (line at 122)
- and the third is biphenyl (line at 154).

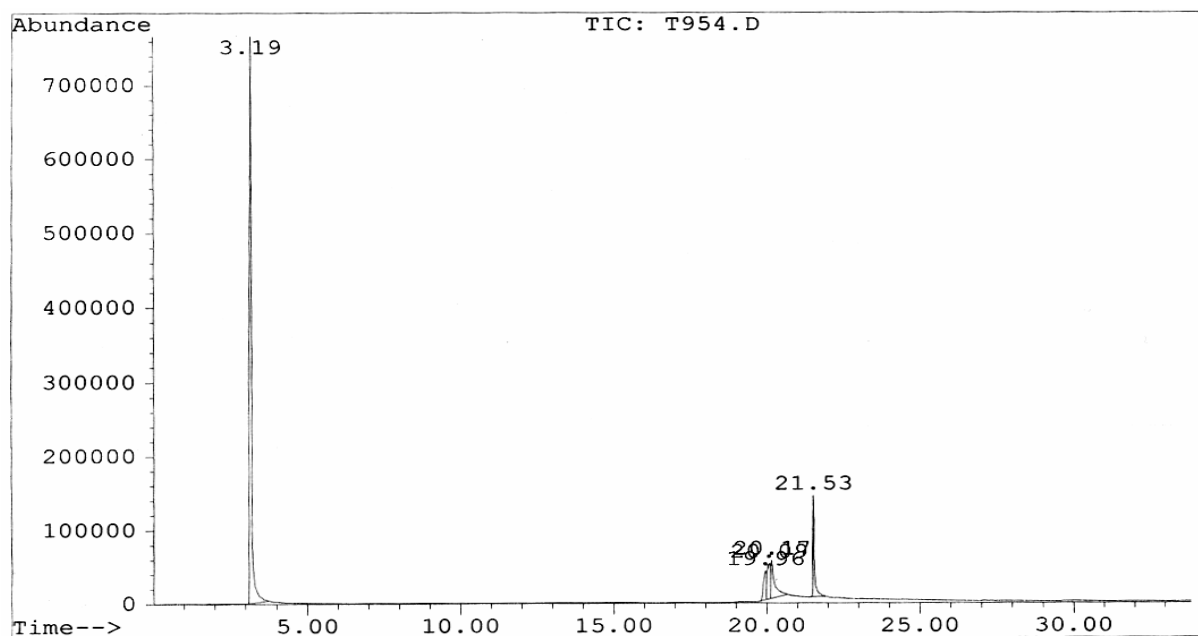


Figure 5 - Chromatography of TA, autoclave treated in the atmosphere of H₂O vapor, 48 hrs, 420⁰C.

We can assume also that CO₂ is liberated as a result of decarboxilation reaction, although such an assumption could not be fixed directly by our method investigation.

From the above mentioned results we can conclude that autoclave treatment at 200-250⁰C of TA, irrespective of initial parameters of terephthalic acid, leads to considerable crystal growth and to the formation of crystals with regular shapes. Further increase of temperature to 300-350⁰C change the form of crystals to particles consisting of unique oriented plates, while at 400⁰C and above we obtain shapeless porous generation of particles. In supercritical water fluid we may assume that the following processes take place:

- condensation of TA with a resultant formation of an anhydride
- TA decomposition to benzene, benzoic acid and biphenyl

Autoclave treatment at moderate temperatures (around 200⁰C) leads to the formation from fine-crystalline or amorphous TA a material with regular facets. This fact may have a principal importance for the further use of these materials.

REFERENCES

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