

THE FORMATION OF AMMONIUM TEREPHTHATATE AND TEREPHTHALATES OF THE I-III GROUPS OF ELEMENTS AS A RESULT OF RECYCLING OF PET ITEMS IN SUPERCRITICAL WATER.

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INTRODUCTION

The utilization of consumed products from polyethylene terephthalate (PET) - bottles, films and fibers is a difficult problem that remains unsolved in the present time. The quantity of used bottles only in Russia achieves tens thousand tons per year and has the tendency of permanent increasing. Burning of wastes in this case is excluded because of toxicity of combustion products. In previous works [1,2] we suggested to follow the autoclave treatment of PET items in different media with consequent dissolving of the autoclaving product in basic solutions after which terephthalic acid (TA) or its salts were obtained.

We investigate depolymerization of PET upon autoclave treatment in basic, neutral and acidic media [2] obtaining, as a result, TA and ethylene glycol (EG). According to the parameters of the process crystals of TA of various size in the range of 3-400 μ are obtained. For the further enhancing of the profitability of the process we suggest to investigate the possibility of obtaining various terephthalates. Usually we rarely find in literature works devoted to the application of terephthalates, though recently this direction begins to develop intensively. The layered structure of terephthalates may determine their application as molecular sieve and absorbents [3]. Terephthalates can also be used as fillers for plastics and in the manufacture of construction materials. Besides, from the thermal disintegrating of TA salts we can get materials with valuable properties we can obtain, in particular, crystals of oxides of the submicronic size.

EXPERIMENTAL PART

In this work we used both commercial TA of high purity and TA obtained by treatment of the consumed products from PET in autoclave, in the atmosphere of water vapor. These two forms of the acid were identical according to results of chemical analysis, X-ray diffraction (XRD), NMR and IR investigations.

The terephthalates were investigated using various chemical and physical-chemical methods – thermal analysis, IR spectroscopy (NEXUS (Nicolet) Fourier transform spectrophotometer on the tablets pressed with KBr) and XRD analysis on a DRON-7 diffractometer (Cu, Ka). Thermogravimetric analysis have been performed on derivatograph Q-1500 D device, MOM with a rate of heating equal 6 deg./min. The elemental analysis of C, H and N was performed using gas chromatography investigation technique on a CHNSO “E” analyzer (Carlo ERBA). The content of metals have been defined by an atomic emission

method and in parallel by chelatometry ethylene diamine tetraacetate (EDTA) volumetric titration. Metal content in terephthalates was determined also by calculating the mass of the residue using TG curves at temperatures of ~1000°C which corresponds to full transition of terephthalate into oxide.

RESULTS AND DISCUSSION

The terephthalates of elements of I-III groups were obtained from ammonium hydroxide solution of ammonium terephthalate by their precipitation due to the addition of salt solutions of these elements. Precipitation of terephthalates of alkaline metals (Na, K) takes place in an excess of ammonium hydroxide. This aspect did not prevent the salt formation since solubility of hydroxides of alkaline metals is quite large under these conditions.

Table 1. Composition of obtained terephthalates

Sample	Contents, mass. %							
	Theoretical				Experimental			
	C	H	Me	O	C	H	Me	O
$\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$	45.71	1.90	21.90	30.47	45.57	1.38	21.03	32.02
$\text{NaC}_8\text{H}_5\text{O}_4$	51.06	2.65	12.23	34.04	51.81	2.51	10.42	35.26
$\text{KC}_8\text{H}_5\text{O}_4$	47.03	2.44	19.15	31.35	47.35	1.86	20.29	30.50
$\text{CaC}_8\text{H}_{10}\text{O}_7$	37.20	3.87	15.50	43.41	37.60	3.73	15.67	43.00
$\text{MgC}_8\text{H}_8\text{O}_5$	42.85	3.57	10.71	42.85	43.17	3.48	10.50	42.85
$\text{Al}_2\text{C}_{24}\text{H}_{28}\text{O}_{20}$	41.73	4.05	7.82	46.37	41.94	3.57	7.38	47.11

Table 2. The intensity (I) and values of d spacing in Å of XRD lines for different terephthalates

$\text{NaC}_8\text{H}_5\text{O}_4$		$\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$		$\text{KC}_8\text{H}_5\text{O}_4$		$\text{CaC}_8\text{H}_{10}\text{O}_7$		$\text{MgC}_8\text{H}_8\text{O}_5$		$\text{Al}_2\text{C}_{24}\text{H}_{28}\text{O}_{20}$		$\text{NH}_5\text{C}_8\text{O}_4$	
d	I	d	I	d	I	d	I	d	I	d	I	d	I
5.53	17	5.16	100	5.40	27	6.97	10	6.07	100	5.37	15	5.68	37
5.07	100	4.67	23	4.55	100	6.61	25	4.77	50	5.04	100	4.60	53
4.67	17	4.10	12	3.49	50	6.15	100	4.53	45	3.52	78	3.73	100
4.33	68	3.71	20	3.40	40	5.83	17	3.97	12	3.19	100	3.51	64
3.48	49	3.56	12	3.12	30	5.34	15	3.55	55	3.01	20	3.41	13
3.45	29	3.30	42	3.06	27	4.98	30	3.07	95	2.80	15	3.07	13
3.19	100	3.14	100	2.82	35	4.80	27	3.00	100	2.73	15	3.05	23
3.12	40	3.08	42	2.73	12	3.66	12	2.64	70	2.67	15	2.90	12
3.01	27	2.92	47	2.60	27	3.58	100	2.57	30	2.53	15	2.62	14
2.91	34	2.82	42	2.33	20	3.12	20	2.36	22	2.26	30	2.27	19
2.80	16	2.71	90	2.22	100	3.02	35	2.28	40	2.19	30	1.83	12
2.71	16	2.60	37	2.17	17	2.88	12	2.22	25	2.13	20		
2.66	30	2.37	100	1.99	25	2.81	35	2.14	40				
2.54	26	2.17	79	1.87	47	2.78	25	2.07	17				
2.26	33	2.03	25	1.82	23	2.30	12	1.94	13				
2.23	25	2.00	22			2.27	85	1.87	45				
2.16	100					2.25	32						
2.01	88					2.17	20						
1.89	23					2.09	17						
1.80	20					1.97	19						

For the preparation of terephthalates of elements of II and III groups (Mg, Ca, Al) the solution of ammonium terephthalate was initially neutralized up to $\text{pH} = 6$. Identification of the obtained compounds have been carried out on the basis of the chemical analysis and X-ray investigation (Tables 1, 2).

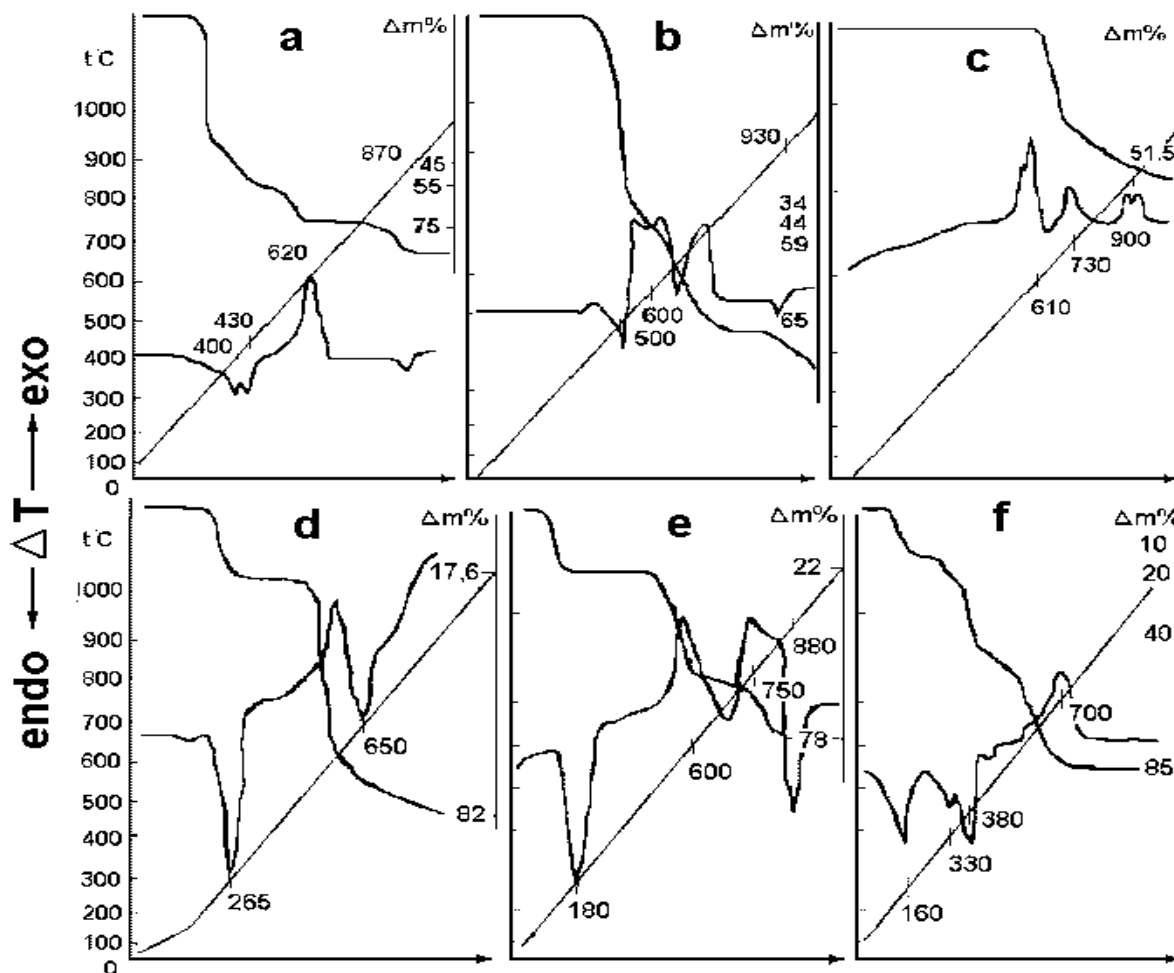


Fig. 1. DTA and TG curves of terephthalates: a – $\text{NaC}_8\text{H}_5\text{O}_4$; b- $\text{KC}_8\text{H}_5\text{O}_4$;
c- $\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$; d- $\text{MgC}_8\text{H}_8\text{O}_5$; e – $\text{CaC}_8\text{H}_{10}\text{O}_7$; f- $\text{Al}_2\text{C}_{24}\text{H}_{28}\text{O}_{20}$
 Δm – loss of mass in %

DTA and TG curves for obtained terephthalates are shown on Fig.1. Upon heating the sample up to 1000°C we notice exothermal effects on all DTA curves, which was accompanied by significant mass loss up to 55%. That may be related to the combustion of organic component of terephthalates. Endothermic effects are defined by loss of internal crystalline water which occurs at temperature below 330°C . Calcium terephthalate loses water in one stage at 180°C with mass loss of 22% that corresponds to 3 molecules of water (Fig. 1e). Magnesium terephthalate also loses water in one stage at 265°C with mass loss of 17% that corresponds to 2 molecules of water (Fig. 1d). Aluminum terephthalate loses 8 molecules of water in two stages: 4 molecules at 160°C and 4 at 330°C (Fig. 1f). For terephthalates of alkaline metals exothermal effects at around 550°C are related to their carbonization. This conclusion arise from literarerature data [4].

For sodium hydrogen terephthalate and potassium hydrogen terephthalate we can distinguish on DTA curves endothermic effects accompanied by a significant loss of mass

(Fig. 1?,b,c): sodium hydrogen terephthalate and potassium hydrogen terephthalate lose 55 % (at 430°?) and 34% (at 500°?) correspondingly. On the DTA curves of K, Na, Al terephthalates small exothermal effects were observed. Formation of carbonates for all investigated terephthalates (except for aluminum terephthalate) is observed at 800°?. At temperatures >800°? carbonates are transformed into corresponding oxides, which are considered to be end-products at 1000°?.

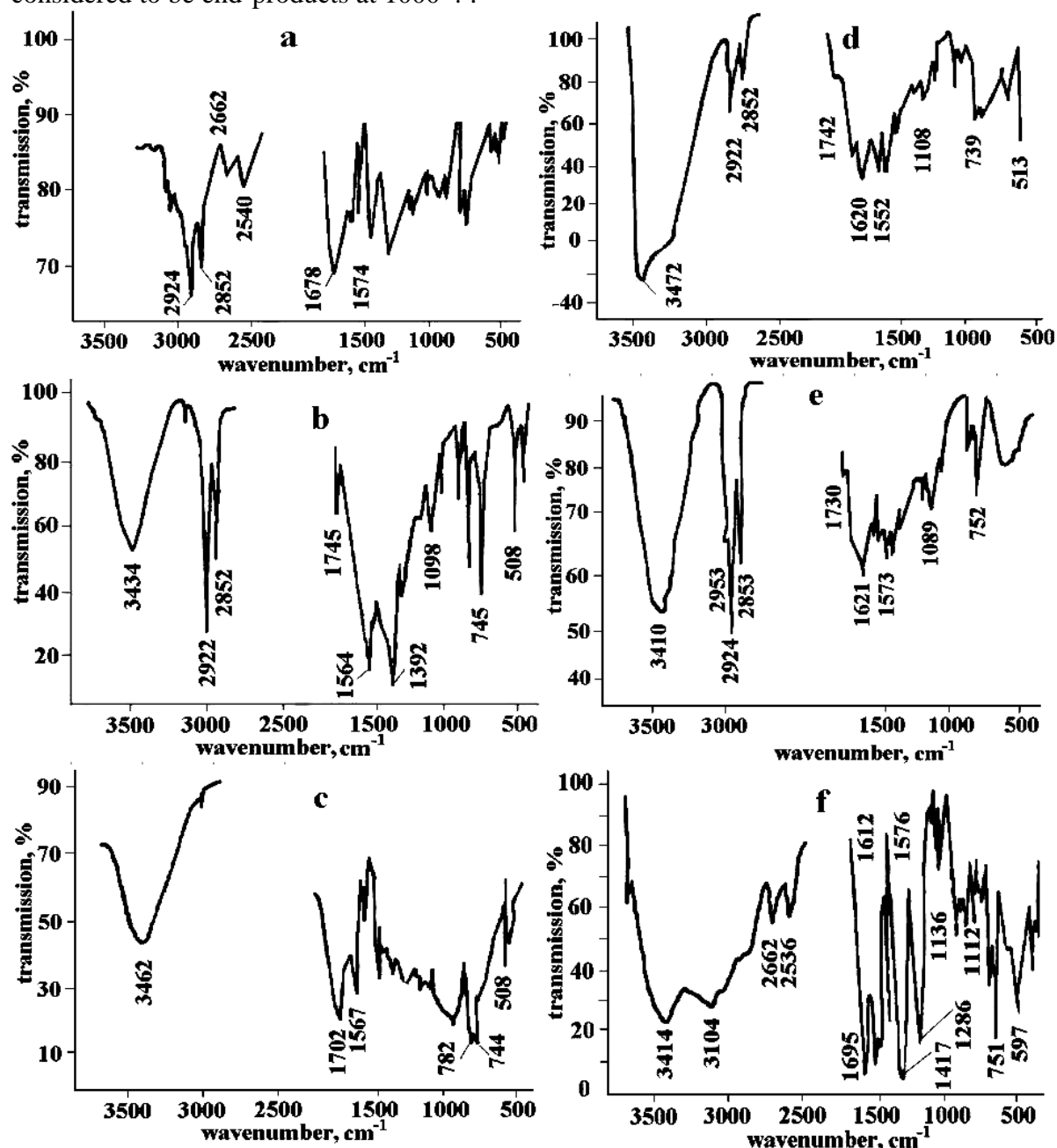


Fig. 2. IR spectra of terephthalates:

- a- disodium terephthalate;
- b- sodium hydrogen terephthalate;
- c- potassium hydrogen terephthalate;
- d- calcium terephthalate;
- e- magnesium terephthalate;
- f- aluminum terephthalate.

IR spectra of investigated terephthalates are represented on fig. 2. For all terephthalates there are wide intensive bands of absorption in the range of $3410-3472\text{ cm}^{-1}$ which belong to stretching vibrations of OH-groups $\nu(\text{OH})$. Shift of the bands towards the low frequency area of the spectrum is related with significant molecular interaction. In spectra of calcium, magnesium and aluminium terephthalates there are bands in the range $1612-1621\text{ cm}^{-1}$, belonging to deformation vibrations of water molecules $\delta(\text{H}_2\text{O})$. That confirms the presence of crystallization water in these salts. Disodium terephthalate has no bands in the range of hydroxyl groups stretching vibrations. In terephthalic acid the bands at 1682 cm^{-1} belong to the stretching vibrations of $\nu(\text{C}=\text{O})$ [5]. For hydrogen terephthalates there is shift of this band towards the low frequency area of spectrum.

The value of $\nu(\text{C}=\text{O})$ for ammonium hydrogen terephthalate, potassium hydrogen terephthalate and sodium hydrogen terephthalate are $1704, 1702$ and 1745 cm^{-1} respectively. All bands are quite intensive, that is related to significant weakening of C=O bond and in accordance with known structural data [6-8]. In disodium, calcium and in magnesium terephthalates the absorption in this area is practically absent, and that is due to the transformation of C=O bond to C-O-Me bond.

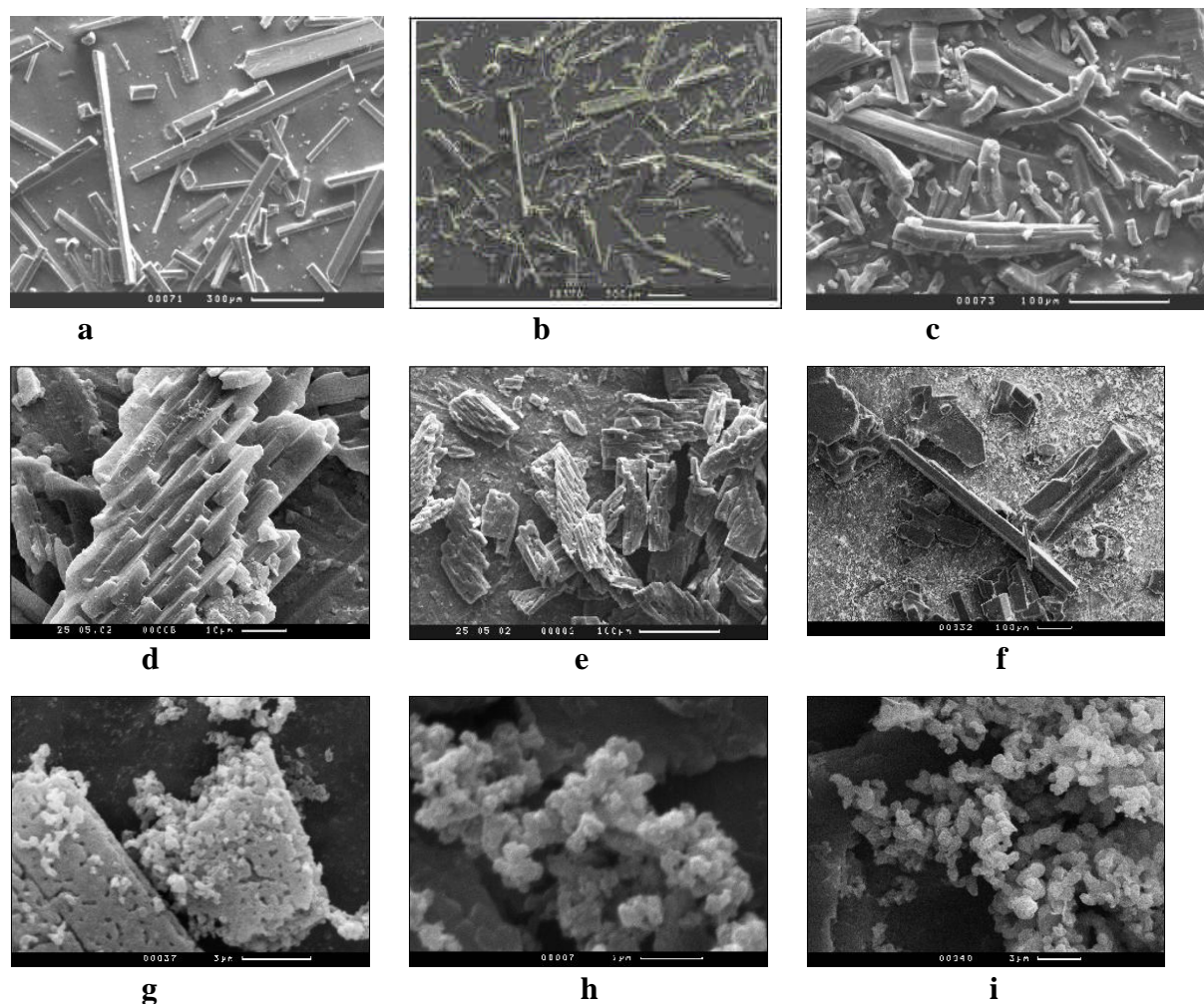


Fig. 3. Electron microscopy of various terephthalates :
a- potassium; b- sodium; c- lithium; d,e- calcium; f,g,h,i- aluminum;
h- after heat-treatment at 700°C for 2 hrs.; i- after heat-treatment at 1000°C for 2 hrs

The mechanism of transformation of the OCO group in the series: PET - TA - TA salts is of a great interest. Stretching vibrations $\nu(\text{CO})$ in the polymer are in the range 1122-1208 cm^{-1} [9,10]. In IR spectrum of PET we find a wide band at 1130 cm^{-1} . Very weak bands are present in TA and aluminium terephthalate (1136 cm^{-1}). Other terephthalates practically have no absorption bands in the given area, and that is due to the absence of polymeric structure.

In fig. 3 electronic microscopy photos of sodium, potassium, lithium, calcium and aluminum terephthalates are illustrated. Microphotos of Na, K, Li salts are almost the same (Fig. 3a,b,c). Similar form is noticed for the crystals of aluminium terephthalate (Fig. 3f) and ammonium terephthalate [11]. Different form occurs for the calcium terephthalate crystals, (Fig. 3d,e) where large secondary structures are observed.

Electronic microphotos (fig. 3h,i) show that the decomposition of aluminum terephthalate after heating at 700 and 1000 $^{\circ}\text{C}$ for 2 hrs. reveals the formation of crystals of aluminum oxide with size less than 1 μ . Further heating at 1000 $^{\circ}\text{C}$ for 2 hours leads to the formation of a crystals of α -alumina.

These results show, that both, commercial terephthalic acid and TA resulted from depolymerization of PET, are suitable for obtaining pure and shaped crystals of terephthalate of elements of I-III groups. Such material can meet wide practical application. In particular, their layered structure with fixed interlayer distances make 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 quite 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.

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