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APPLICATION OF THERMAL ANALYSIS PROCEDURES TO THE STUDY PYROLYTIC AND FLAMMABILITY OF SOME POLYMERS

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ABSTRACT

Thermoanalytic measurements of some polymers were done in dynamic atmosphere of oxygen, air or nitrogen. Entalpic values were calculated from the peak areas of DTA-curves. These results are compared with both: - the calorimetric measurements in oxygen bomb and - the results of another flammábility tests of polymers.

The enthalpic values, obtained in the open system of thermoanalyzer are much lower, than the values determined in calorimetric bomb. The main part of volatile products from pyrolysis of polymers is not oxidized even in flow of pure oxygen. The heat of combustion /determined thermoanalytically/ is higher in the case of polymers forming char residues, which are combusted in two stages.

INTRODUCTION

The flammability of natural and synthetic polymers is often evaluated in accordance with combustion heat values. These values are determined in oxygen bomb, at static atmosphere of pure oxygen, under the pressure /p = 3 MPa/ /ref. 1 and ref.2/. These values are not in acceptable correlation with the observation at real fires /ref.1/. Polymers which have similar values of heat of combustion /similar chemical composition/ might burn with very different burning rate. Fire retardancy has very small effect on the determined heat of combustion.

Differential thermal analysis /DTA/ provide semiquantitative information on heat balance when polymer is heated at definite conditions. Several elementary proceses take place prior of flaming or not-flaming combustion of polymers /e.g. melting, thermolysis, evaporation of volatile primary products/. These

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reactions are endothermic, but /in the oxygen atmosphere/ are rapidly followed by secondary exothermic reaction. Thermal analysis gives a possibility to study of individual stages of the combustion process /ref.3/.

METHODS

The complex thermoanalytical investigations /DTA, TG-DTG/ was carried out with a Mettler-TA-1 analyzer under following conditions: samples weight 100 mg, ceramic crucible, heating rate 10 $deg.min^{-1}$, top temperature 800 ^{o}C, reference material Al_2O_3, thermocouples Pt/Pt+Rh, Dynamic gas /N_2, air, O_2/ atmosphere 7 $l.h^{-1}$. The scale sensitivity 100 $\mu V/254$ mm.

The standard suggested by the standardisation commitee of ICTA were employed for the heat and apparatures calibration /ref.4/. Heat of reactions were calculated by Simpson method of numeric integration of DTA-curves. Program ML-09 of standard softwar integrated modul and the programable calculator TI-59 were used.

Oxygen index /OI/ was measured with a Stanton Redcroft FTA oxygen index unit /ASTM D-2863-77/. Heat of combustion /ΔH comb./ were determined in a Bertholet-Mahler bomb calorimeter /ASTM D-271-64/. The flash ignition temperature /FIT/ and selfignition temperature /SIT/ of samples were determined in the Setchkin apparatus with an air flow velocity in the furnace of 25,5 $mm.s^{-1}$ /ASTM D-1929-68/.

RESULTS AND DISCUSSION

All values of thermoanalytically determined enthalpies /Table 1/ are much lower than those obtained in closed system of oxygen bomb. In the open system more than 90 % of heat is probably lost with primary volatile product of pyrolysis. It is also possible that primary products are not completly oxidized even in the flow of pure oxygen during DTA analysis. Some of tested polymers /polyacrylonitrile, polyvinylchloride, polycarbonate, polyamide/ form the char at used conditions. Main part of heat is evolved during the consecutive oxidation of the char, /Table 2/.

The substantial differences in values of enthalpy were determined in both atmosphere of nitrogen and in oxygen flow. These differences are characteristic for such polymers as polyethylene and polypropylene. DTA-curves for several polymers /oxygen containing polymers, PVC, PAN/ are slightly exothermic in the nature, although the nitrogen flow is used during the analysis /Table 2/.

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TABLE 1

Some flammability parameters
and results of enthalpic measurements

Sample	OI /Vol.%O_2/	FIT /^oC/	SIT /^oC/	Oxygen bomb ΔH comb. /$kJ.gm^{-1}$/	DTA ΔH /$kJ.gm^{-1}$/
Polyethylene Bralen RB 0223	17,8	355-365	380-390	46,7	2,58
Polypropylene Tatren TF-411	18,0	335-340	400-410	46,4	4,39
Polystyrene Krasten 127	19,3	370-375	450-460	37,5	1,22
Polyethylene-Terephtalate	22,1	390-400	485-500	22,6	0,62
Polyamide Silamid 6	23,8	395-400	465-470	22,6	0,47
Polyacrylonitrile Courtelle	18,2	208-212	495-500	31,5	3,05
Polycarbonate Lexan 500	25,5	455-460	575-580	29,0	0,33
Polyvinylchloride Sloviplast 702	25,7	400-410	440-450	24,3	1,15

TABLE 2

The effects of various atmosphere on the reaction heats /determined semiquantitatively from DTA/

Polymers	Atmosphere	Melting /J.gm^{-1}/	Pyrolysis/ combustion /kJ.gm^{-1}/	Char oxidation
Polyethylene Bralen RB 0223	N_2	45	+ 0,15	-
	air		- 1,19	-
	O_2		- 2,38	-
Polypropylene Tatren TF	N_2	54	+ 0,25	-
	air		- 0,88	-
	O_2		- 4,39	-
Polystyrene Krasten 127	N_2	-	+ 0,49	-
	air		- 1,09	- 0,51
	O_2		- 1,22	- 0,64
Polyethylene-Terephtalate	N_2	38	- 0,52	-
	air		- 0,54	- 2,51
	O_2		- 0,62	- 2,52
Polyamid Silamid 6	N_2	73	- 0,05	-
	air		- 0,28	- 0,53
	O_2		- 0,47	- 0,47
Polyacrylonitrile Courtelle	N_2	-	- 1,21	-
	air		- 2,10	- 1,27
	O_2		- 3,05	- 7,15
Polycarbonate Lexan 500	N_2	-	- 0,08	-
	air		- 0,29	- 2,51
	O_2		- 0,33	- 3,33
Polyvinylchloride Sloviplast 702	N_2	-	- 0,14	- 0,11
	air		- 0,98	- 2,57
	O_2		- 1,15	- 2,82